Investigation on structural, optical, mechanical and NLO properties of a new crystal from amino acid family

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Abstract

In the present work we are reporting the synthesis and growth of single crystal of L-Ornithine phthalate mono hydrochloride by the solvent evaporation method. The grown crystals were characterized by spectroscopic and analytical methods. The crystal parameter was computed from powder x-ray diffraction analysis. The vibrational spectroscopy confirms the presence of functional groups and the thermal stability of the sample was analyzed by TG/DTA curves. The mechanical strength of the grown crystal was found out using a Vickers microhardness test. UV- Vis spectroscopy shows the optical property of the crystal. The lower cutoff wavelength observed around 282 nm indicates that the grown sample is a potential material for SHG application. The real and imaginary part of dielectric constant of the crystal were determined. Frequency conversion efficiency was tested by using the powder Kurtz method, keeping KDP as a reference material.
Keywords: Growth from Solutions; Thermal Analysis; Optoelectronic devices., Path.

1 Introduction

Nonlinear optical materials play a vital role in the modern technologies such as photonics, high speed optical communication, optical parallel information processing telecommunication and optical computing [1,2]. In recent decades, generation of coherent blue light through SHG from near infrared (NIR) region is a big technological challenge. Many researchers are working on this aspect to fabricate single crystal of nonlinear optical materials which give a dramatic contribution to this evaluation [3]. Amino acids are interesting and potential materials for nonlinear optical applications [4]. The salts of L-ornithine amino acids contain a deprotonated carboxylic group $[COO^-]$ and two protonated amino group $[NH^{3+}]$ [5, 6]. Generally in a crystal structure, L-ornithinium occupies as a charged zwitterion with two positive and one negative charge [7, 8]. L- Ornithine mono hydrochloride (L-OMHCl) and L-Ornithine Hydrogen Bromide (L-OHB) are the amino acids group which find applications in optoelectronics and photonics. NLO efficiency of L-OMHCl has been reported as 1.25 times that of KDP [9, 10]. Phthalate based crystals are well known for their high piezoelectric coefficients with acousto-optical interaction [11, 12]. It makes them incredibly useful material for data processing and intra laser modulation in various acousto-optical devices. In this present work, for the first time we have synthesized a new
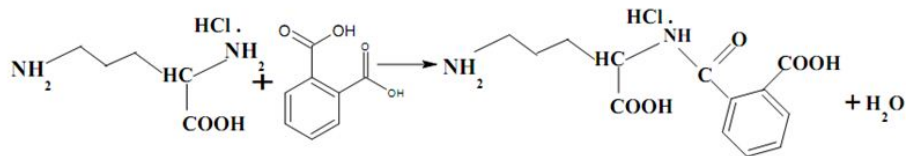
Figure 1: The formation of L-OPMHCL

semi-organic nonlinear optical material L-Ornithine phthalate mono hydrochloride (L-OPMHCl) by dissolving L-Ornithine mono hydrochloride and phthalic acid in deionised water. The single crystal of L-OPMHCl was grown by solvent evaporation technique. L-OPMHCl crystal has carboxyl group, two amino nitrogen atoms and the aliphatic side chain along with phthalate and it builds a charge transfer path between donor and acceptor atoms [13]. Further the grown crystals were subjected to various characterizations to analyze their structural and optical properties. The results were provided in detail in the following section.

2 Experimental work

2.1 Synthesis

L-Ornithine phthalate mono hydrochloride compound was synthesized by dissolving stoichiomatric amount of L Ornithine mono hydrochloride (SLR 99 % and Phthalic acid (SLR 99 %)in deionized water. The solution was stirred well for about 3 hours to maintain homogeneity. The chemical reaction taken place in the process is provided as follows. Fig.1.

L - Ornithine mono hydrochloride + Phthalic acid = L - Ornithine phthalate mono hydrochloric acid

$$C_5H_{12}N_2O_2.HCl + C_8H_6O_4 = C_{13}H_{17}ClN_2O_5 + H_2O$$

2.2 Growth of L-OPMHCl single crystals

The synthesized compound was recrystallized two times and used for the growth of single crystals of L-OPMHCl. The solvent used for the growth of L-OPMHCl crystals is water. 200 ml saturated solution of L-OPMHCl was prepared and the solution was filtered using Whatman No.1 filter paper. Growth has been initiated by the fast evaporation of water which lead to the supersaturation. The seed crystals were grown in 20 days of the time period. The yielded good quality of optically clear and macro defect free seed crystal was used for growth experiment. The L-OPMHCl crystal with the dimension of 6mm x 5mm x 4mm was harvested and is shown in Fig.2.

3 Results and discussion

3.1 Powder X-ray diffraction analysis

Powder X-ray diffraction patterns of L-OPMHCL recorded by an Xpert pro X-ray diffractometer with CuKα (λ = 1.5408 Å) radiation are shown in Fig. 3. All the observed
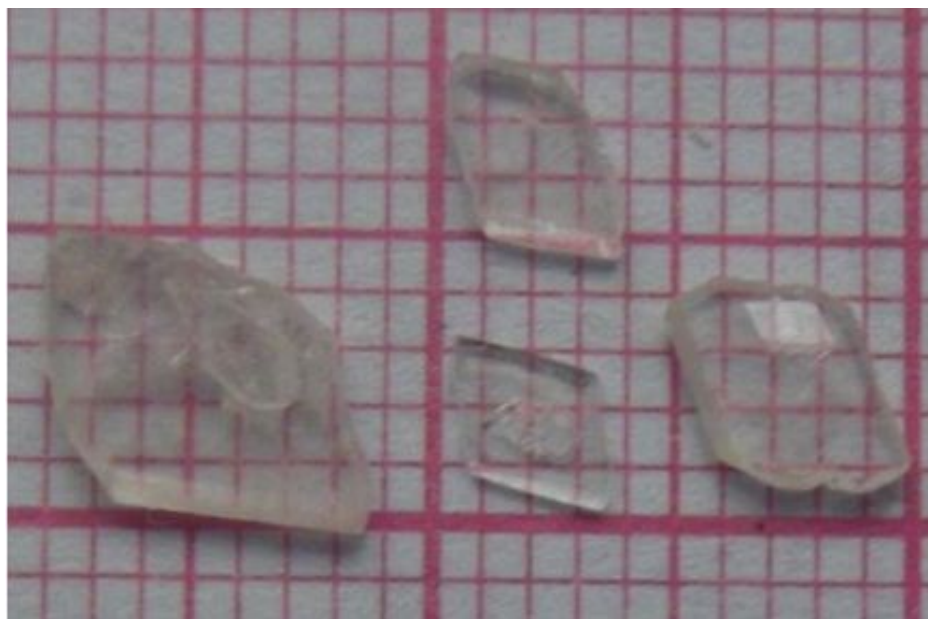
Figure 2: Photograph of as grown crystal of L-OPMHCl

reflections have been indexed and the lattice parameters were calculated as a=8.8785 Å, b=8.8754 Å, c=8.541 Å, $\alpha = \beta = \gamma = 90^0$ and a volume of $673.19mm^3$ with the space group of P4/mmm using full proof suit software. Sharp peaks of XRD pattern indicate higher degree of crystalline structure of grown crystals. The calculated crystal parameters of L-OPMHCl are compared with parameters of L-Ornithine mono hydrochloride (L-OMHCl) single crystals and are shown in Table 1.

3.2 FTIR vibrational spectroscopy study

The FTIR analysis was carried out using NICOLET 185i D1 transmission spectrometer by KBr pellet technique in the mid IR range of $400cm^{-1}$ to$4000cm^{-1}$. The recorded FTIR spectrum of sample crystal is given in Fig. 3. The peak assignments are given in Table 2. While analyzing FTIR vibrational peak of C(=O)OH group, it is good to start with OH stretch. A broad peak found at $3018cm^{-1}$ indicates the OH stretching. The peak found in the middle of the spectrum around $1680cm^{-1}$ has been assigned to C=O stretch. The broad envelope between 3200 and $2500cm^{-1}$ with multiple peaks confirms the presence of amino group $NH2^+$ stretch. The characteristic vibration of the COO^- moiety was found at $673cm^{-1}$. The strong peak determined at $1491cm^{-1}$ is due to symmetric NH^{2+} deformation. The C-C stretching vibrations of the grown crystal appears at $1404cm^{-1}$. The presence of C-Cl group rise to band at $796cm^{-1}$. Thus the presence of functional groups was conformed qualitatively.

3.3 Thermal Analysis on L-OPMHCl

To analyze the thermal stability of grown crystals, the DTA/TGA analyses were carried out between the temperature 0 ^{0}C and 600 ^{0}C in the nitrogen atmosphere at heating rate 10 K/min using Netzsch STA 409 c/cd thermal analyzer. The DTA/TGA curves of L-OPMHCl are shown in Fig. 5. The DTA curve shows a sharp endothermic peak, which corresponds to the melting point of the compound at 220 ^{0}C. The sharp peak indicates the concurrent melting of grown crystals. TGA curve shows that decomposition of the

Table 1: lattice parameters of grown crystals

parameters	L-Ornithine mono hydrochloride[9]	L- Ornithine phthalate monohydrochloride
a	10.1680	8.8785
b	8.2195	8.8785
c	5.0157	8.541
α	90°	90°
β	90°	90°
γ	82.19°	90°
Crystal system	Monoclinic	Tetragonal
Space group	P12$_1$ 1	P4/mmm

Table 2: FTIR spectral data of L-OPMHCL

Wave number (cm^{-1})	Assignments
3018	OH Stretching
3018	OH stretching
2652	NH_2 asymmetric stretching
2521	NH_2 symmetric stretching
1680	C=O stretching
1585	C=C stretch (aromatic)
1491	NH_2 symmetric deformation
1404	C-C stretching (aliphatic)
1284	CH_2twisting
1139	NH2 rocking
1142	C-C stretching
1070	C-N stretching
973	CH deformation
796	C-Cl stretching
673	COO^- stretching
558	NH_3 torsion
445	COO rocking

L-OPMHCl compound has taken place in a single stage. From TGA curve it is clear that the L-OPMHCL crystal has good thermal stability up to 190^0C as there is no major weight loss below that temperature. However, it shows the more weight loss of 95% after the melting point due to the removal of volatile substances. Thus, it confirms the full degradation after 300 ^{0}C.

3.4   Vickers micro hardness

An important use of microhardness study is the possibility of making an indirect estimate of other mechanical characteristics of materials having a specific correlation with their hardness. Transparent and crack free crystals were chosen for hardness measurements. The crystal was then subjected to vickers microhardness test using HMV. 2T shimdazu instrument and the Vickers hardness number H_v is calculated using the relation

$$H_v = 1.8544.\frac{P}{d^2} \qquad (kg/mm^2) \tag{1}$$

Where d is the diagonal length of the indentation and P is the applied load in gram. The variation of H_v for various loads is shown in Fig.6. The Vickers microhardness test revealed that at lower loads harness is relatively high and it declines for higher loads upto 100g. The bond energy of the crystal is believed to cause the higher hardness values at lower loads. The work hardening coefficient or Mayers index n, which relates the applied load and indentation diagonal length, was calculated from Mayers [14] relation P=Kdn or log P= log K + n log d, where K is the material constant. If n is less than 2, the hardness number decreases with increasing load and if n is greater than 2, it increases with increasing load. Therefore according to Onitsch [15] the value of n should lie between 1 to 1.6 for hard materials and for soft materials it should be above 1.6. By plotting the graph of log p versus log d Fig.7, the value of work hardening coefficient n has been determined and is found to be less than 1.6, which confirms that the crystal belongs to category of hard material.

3.5   Determination of optical constants

The grown sample L-OPMHCl has low absorbance in the UV-visible region. A potential non linear optical material should have high transmission, low reflectance and low refractive index. In order to understand the band structure and the type of transition of electron existing in the grown sample the absorption coefficient (α), extinction coefficient (K), reflectance (R) and refractive index (n) were calculated and further it was extended to compute the optical conductivity and electrical conductivity of L-OPMHCl crystals. All the linear optical constants were determined using the theoretical expressions. The optical absorption coefficient has been calculated from the relation [17]

$$\alpha = \frac{1}{t}.2.303 log\frac{1}{T} \tag{2}$$

where t thickness of the crystal and T is the percentage of transmittance% . The absorption coefficient depends on the material and also on the wavelength of light which is being absorbed The extinction coefficient [18] is given by

$$k = \frac{\alpha\lambda}{4\pi} \tag{3}$$

Reflectance can be calculated in terms of absorption coefficient as

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

The refractive index of the material in terms of reflectance is given by the relation [19,20]

$$n = \frac{-(R+1) \pm \sqrt{3R^2 + 10R - 3}}{2(R-1)} \qquad (5)$$

The above calculation gives the refractive index of the L-OPMHCl crystal as 1.92. The dielectric constant of L-OPMHCl was calculated as 3.8 by the summation of ε_r and ε_i where

$$\varepsilon_r = n^2 - K^2 \qquad (6)$$

the real part of dielectric constant and

$$\varepsilon_i = 2nK \qquad (7)$$

imaginary part of dielectric constant. Optical conductivity of the material in terms of absorption coefficient and refractive index has been calculated using the relation [21, 22]

$$\sigma_{op} = \frac{\alpha n c}{4\pi} \qquad (8)$$

Electrical conductivity of the material in terms of measure of optical conductivity is given by as

$$\sigma_e = \frac{2\lambda \sigma_{op}}{\alpha} \qquad (9)$$

The relation between the optical and electrical conductivity is plotted in a graph and is shown in Fig.10. From the graph it is observed that the optical absorption as a function of wavelength of the grown crystal is high at lower wave length region further it decreases exponentially with increase of wave length. However the electrical conductivity of the sample is low at lower wavelength region and it increases with the increase of wavelength.

3.6   Dielectric Studies on L-OPMHCl Single Crystals

The dielectric property reveals how easily a material can become polarized by the application of an electric field. Measurement of dielectric constant or electrical permittivity and dielectric loss are vital in the design of nonlinear optical devices since they are interrelated to electro optic properties of the material. In our work the crystal with the dimension of 2.5 x 2 x 0.7 mm^3 was used for the study of dielectric properties. The dielectric constant and the dielectric loss of L-OPMHCl crystal were measured using 4284A LCR METER. The studies were carried out at three different temperatures 313 K, 333K and 353 K for frequencies varying from 100 Hz to 1 MHz. The results are plotted and are shown in Fig.11 and Fig.12 respectively.

The dielectric constant of L-OPMHCl crystal was calculated using the relation

$$c = \frac{\varepsilon_r \varepsilon_0 A}{d} \qquad (10)$$

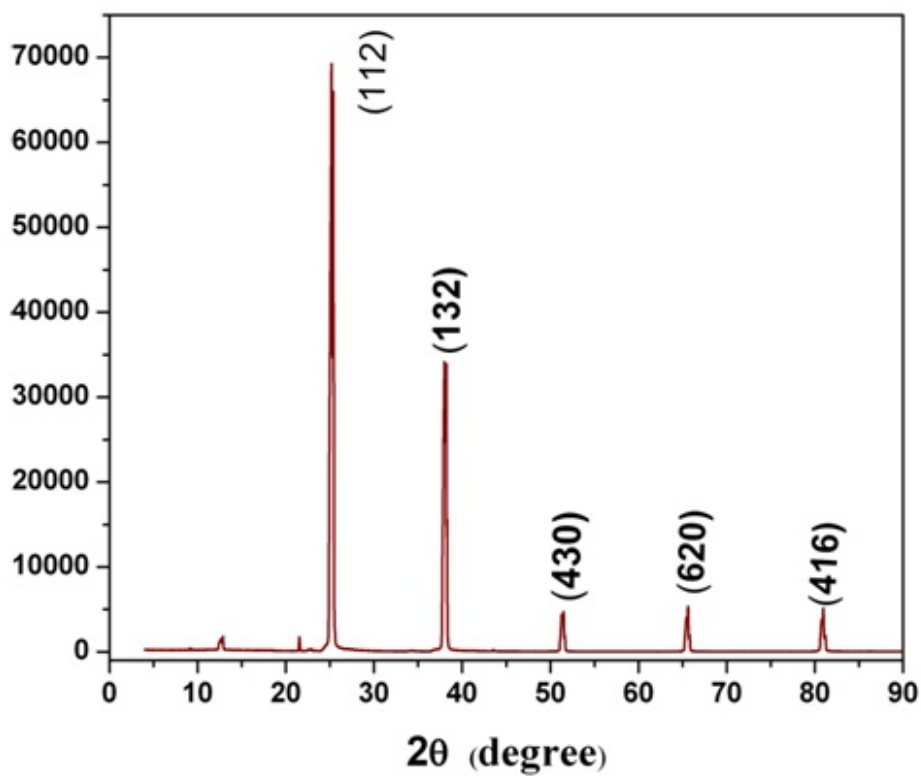$$\varepsilon_r = \frac{cd}{\varepsilon_0 A} \qquad (11)$$

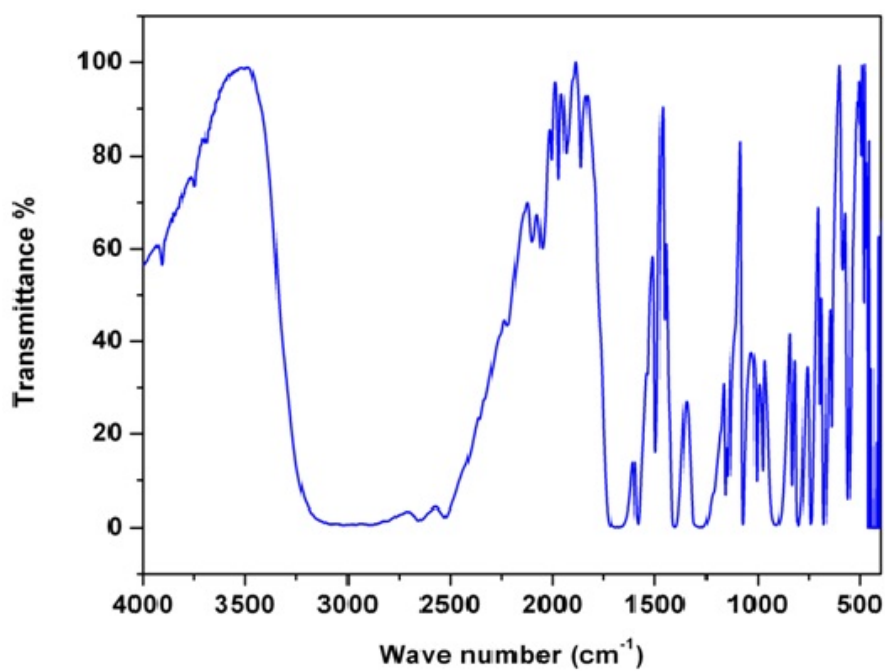Figure 3: Powder XRD pattern of L-OPMHCl
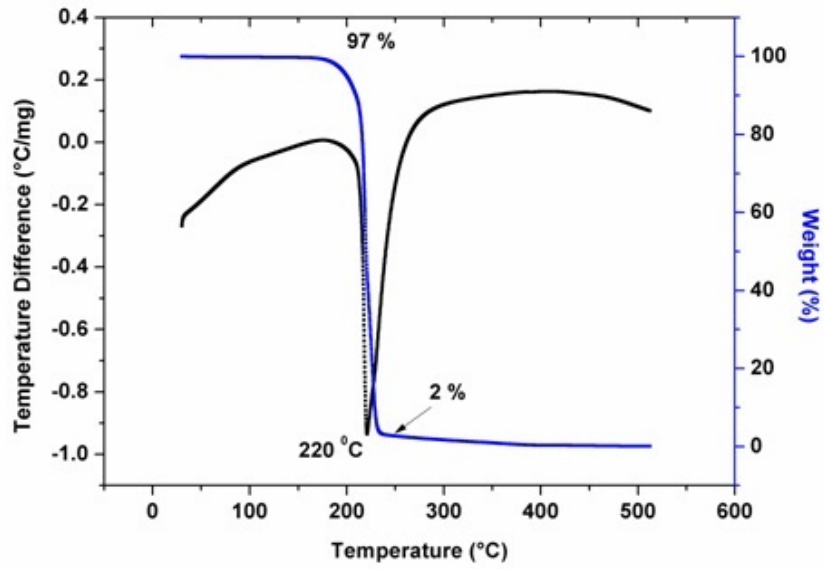

Figure 4: FTIR spectrum of L-OPMHCL

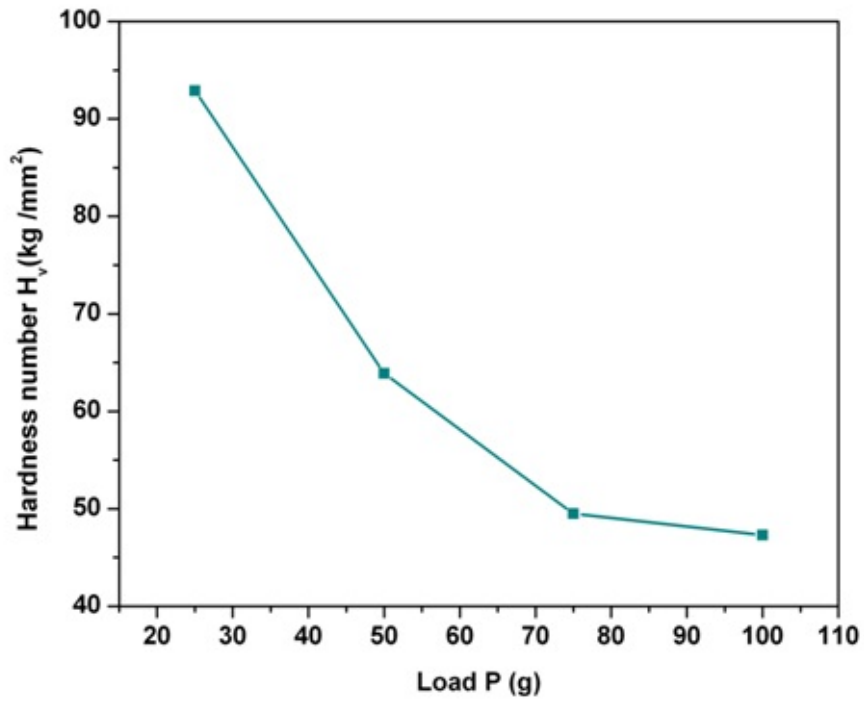Figure 5: TG/DTA analyses on L-OPMHCl single crystals

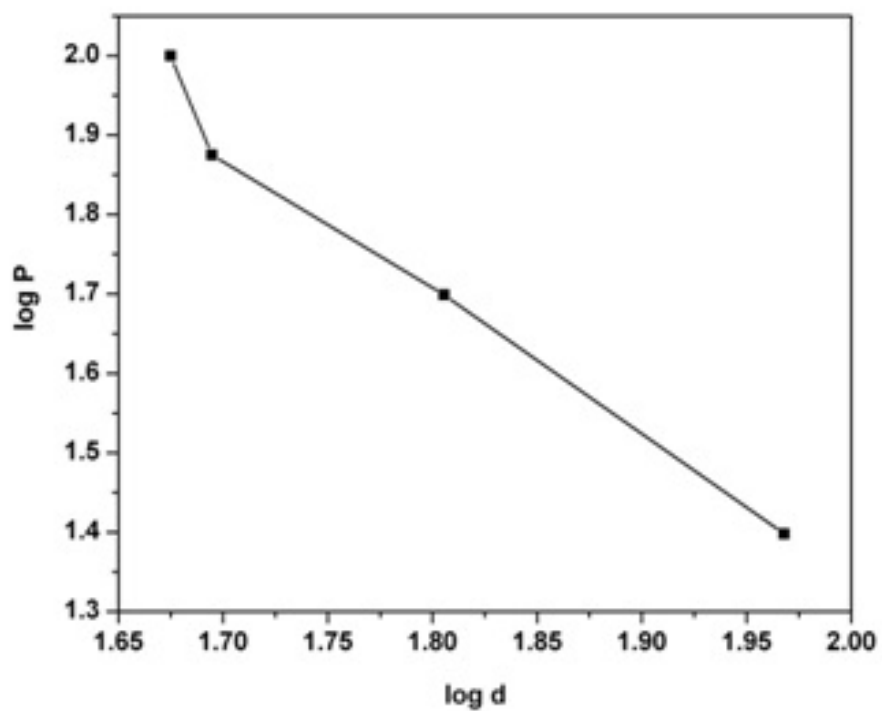Figure 6: Variation of Vickers hardness number with load P
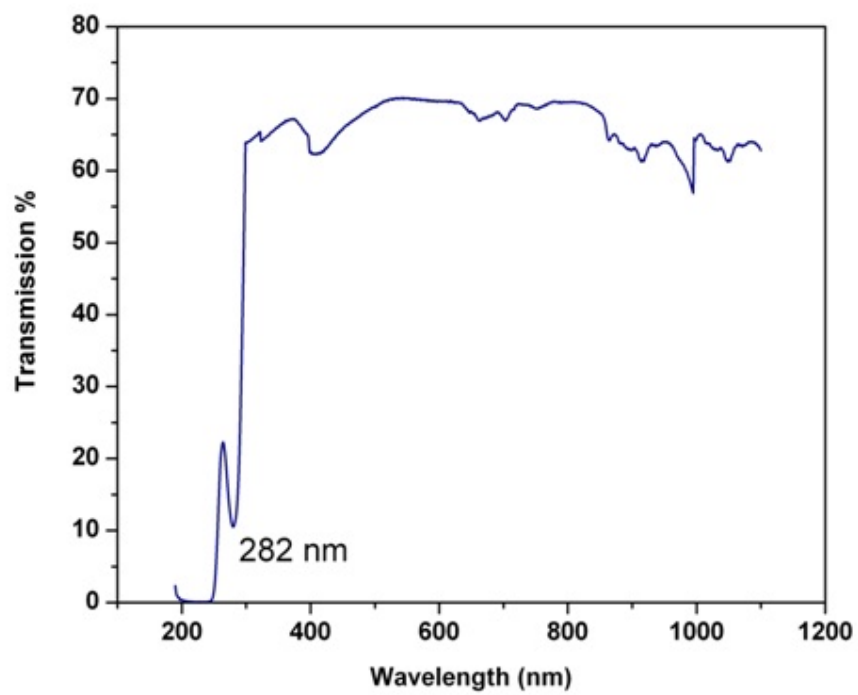
Figure 7: Plot of log p against log d

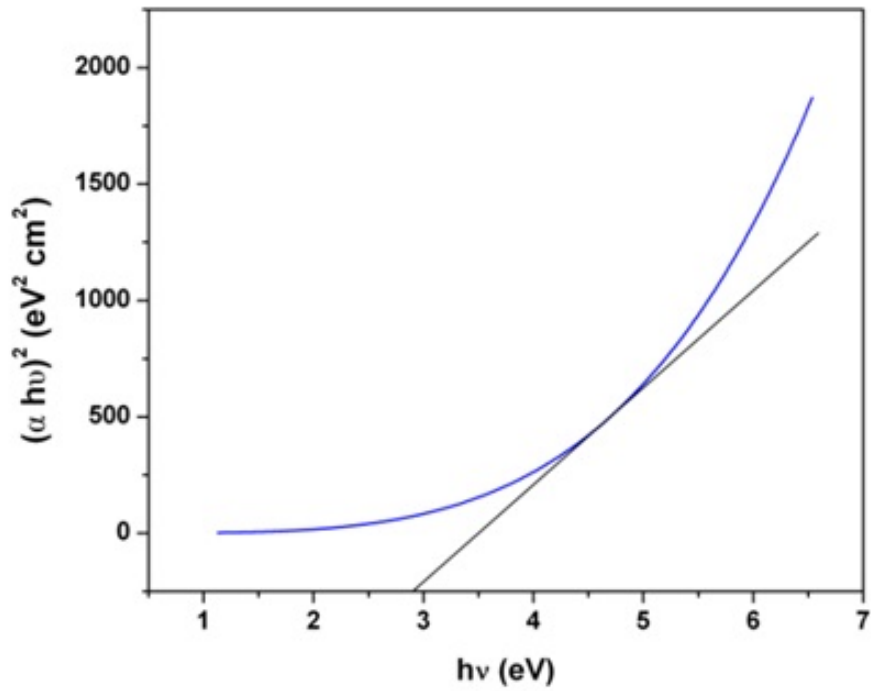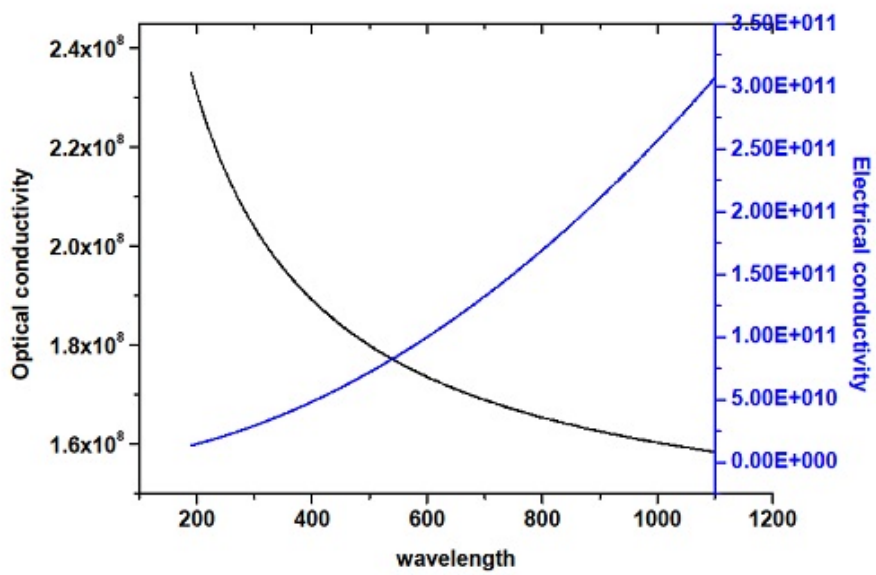Figure 8: UV-Vis-NIR Spectrum of L-OPMHCL

Figure 9: Taucs plot for L-OPMHCL

Figure 10: Relation between Optical conductivity and Electrical conductivity
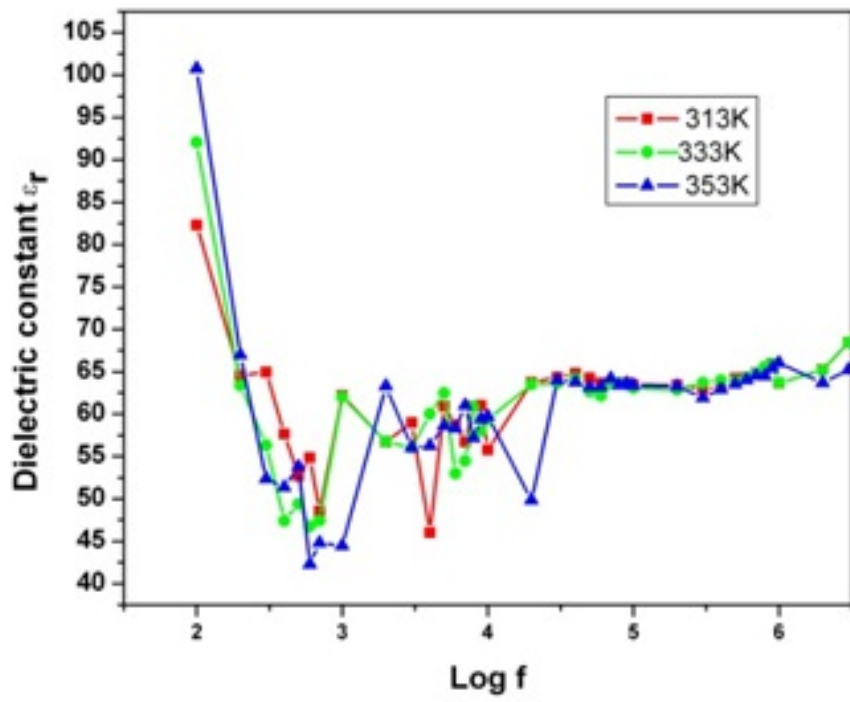
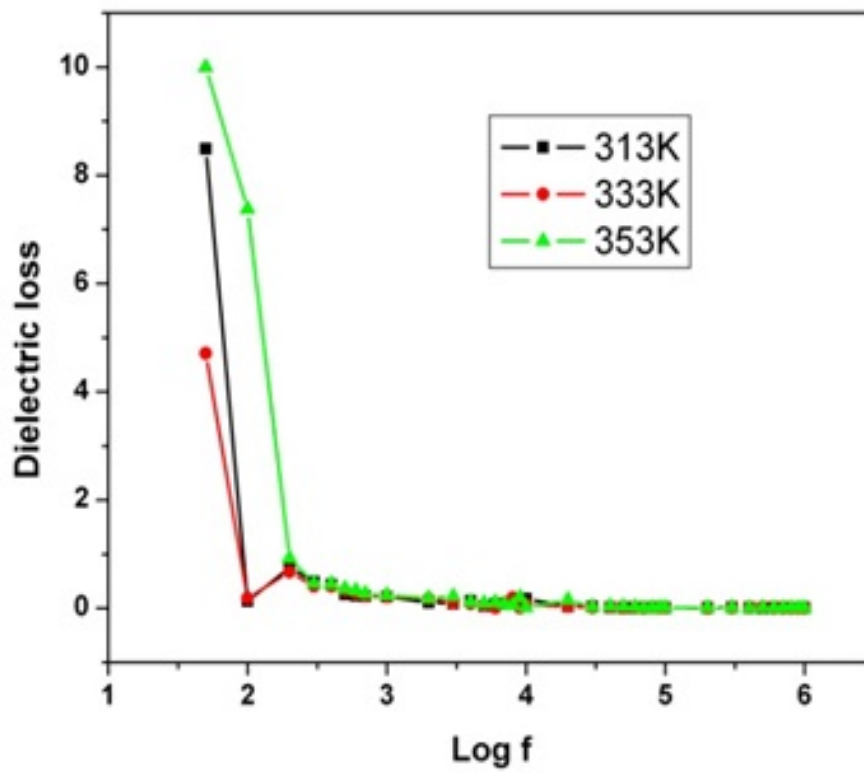Figure 11: Variation of dielectric constant with Log f

Figure 12: Variation of dielectric loss with Log f

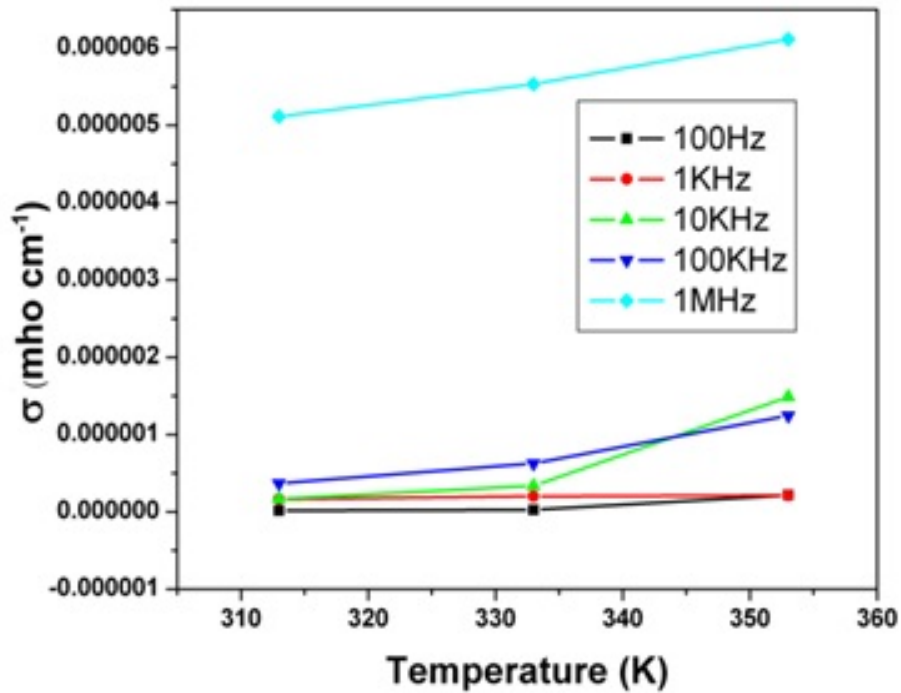Figure 13: Temperature Vs Conductivity

where, ε_0 is the permittivity of free space and ε_r is the relative permittivity or dielectric constant of the material (a number without dimensions). From the graph, we found that the crystals showed quite high dielectric constant only at low frequencies such as 102 at a temperature of 353 K. After that the dielectric constant begins to decrease then at the mid frequency range it remains constant because of loss of all four polarizations. The dielectric loss $\tan\theta$ was also studied for various frequencies and it is observed that dielectric loss has high values in the lower frequency region and lower values in the higher frequency region. The low dielectric loss with a high frequency of the crystal shows that the crystal possesses good optical quality with less defects and this parameter play a vital role in the fabrication of nonlinear optical applications [23, 24, 25]. The electrical conductivity of materials depends transport of ions and electrons. In dielectric materials there are plenty of electrons but they cant move. Fig.13 shows the increase in ac conductivity while temperature increases since its band gap value is 2.9 eV.

3.7   SHG efficiency

The conversion efficiency for the second harmonic generation of the grown L-OPMHCl crystal was carried out by Kurtz-Perry technique [26] since it is crystallized with noncentrosymmetric space group. The crystals of L-OPMHCl were ground to a uniform particle size and then exposed to and: YAG laser beam of 1064 nm wavelength. A powder of potassium dihydrogen orthophosphate (KDP), with the same particle size, was used as the reference. A laser input of 8.8 mg was passed through the L-OPMHCl powdered sample and second harmonic signal of 4.6 mJ was obtained. From this measurement, it is found that the SHG efficiency 0.52 times than of the KDP crystal.

3.8 Conclusions

Single crystals of L-OPMHCL were grown by the slow evaporation technique at room temperature and its properties are analyzed through various characterization techniques. Unit cell parameters were evaluated by X-ray diffraction analysis, which confirmed that the grown crystal belongs to the tetragonal system with space group P4/mmm. FTIR spectroscopy analyzes were done to identify the presence of respective functional groups in the grown crystals. The sharp endothermic peak of DTA curve at 220^0C gives the melting point of grown crystals. The hardness study implies the decreasing nature of hardness number with the increase in load. Hardness investigation makes known that L-OPMHCl crystal belongs to a hard material category. The optical absorption analysis shows that grown crystal has wide transparency window in the entire UV-visible and IR regions with a lower cutoff wavelength at 282 nm. The optical constants were determined. The Kurtz powder technique indicates that the SHG efficiency of L-OPMHCL is 0.52 times that of KDP. As the crystal has wide transparency in the UV and visible regions, low dielectric constant, low dielectric loss and good mechanical properties, L-OPMHCl crystal can be used as a potential frequency conversion material.

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