



## STRUCTURAL, OPTICAL, DIELECTRIC AND HARDNESS STUDIES OF L-HISTIDINIUM CRYSTAL

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**ABSTRACT** L-histidinium methyl ester dihydrochloride ( $C_7H_{11}N_3O_2 \cdot 2HCl$ ), a semi-organic nonlinear crystal of L-histidine family was grown by slow evaporation method at room temperature. X-ray diffraction and FT-Raman spectral studies were employed on the grown crystal for structural analysis. The optical spectral study was performed to know the optical transmittance of the grown compound in the visible and UV regions. Powder technique of Kurtz and Perry was employed to study the harmonic generation efficiency of the L-histidinium methyl ester dihydrochloride single crystal. The dielectric study was performed and the parameters such as dielectric loss and dielectric constant were studied. AC conductivity studies were performed. The mechanical behaviour of the grown crystal was studied using Vickers microhardness tester and the results are discussed.

**KEYWORDS** : Single crystal, XRD, FT-Raman, Optical, dielectric, Microhardness.

## INTRODUCTION

New types of nonlinear optical crystals are much needed in technological applications due to the fact that bulk growth of semi-organic crystals in all three dimensions makes the crystal growth process easy and suitable for device fabrication [1]. It is well known that semiorganic crystals possess the strong nonlinear optical properties and chemical flexibility of organic materials and the physical sturdiness and excellent transmittance of inorganic counterparts [2–4]. However, enhancement of nonlinear optical properties of semi-organic crystals plays the major role of investigation due to the added advantages of both organic and inorganic crystals. It is of great interest to grow semiorganic crystals using amino acids with inorganic or metal complexes to enhance their physicochemical properties [5].

It is well known that amino acids are most suitable materials for nonlinear optical applications as it contains an asymmetric carbon atom which makes them optically active and also most of them except glycine, crystallize in non-centrosymmetric space groups. In recent times, plentiful investigation have been carried out to synthesize amino acid mixed organic and inorganic materials with improved chemical stability, optical, thermal, electrical, mechanical properties apt for nonlinear optical applications [6–8].

Semiorganic crystals of L-histidinium family such as L-histidinium monohydrochloride phosphate, L-histidinium cadmium chloride monohydrate and L-histidinium nitrates have been already grown and reported by quite a few authors and these materials were found to be nonlinear materials suitable for photonic applications [9–11]. Inspired by the preceding works, we have grown a semi-organic salt of  $C_7H_{11}N_3O_2 \cdot 2HCl$  (LHMED) suitable for photonic industry applications. The preliminary structural studies of LHMED were already reported by Victor H. Vilchiz et al [12] and had been already identified as a potential material for optical applications. In our present study,  $C_7H_{11}N_3O_2 \cdot 2HCl$  crystals were grown and subjected to FT-Raman spectral studies, optical studies, electrical and mechanical studies.

## EXPERIMENTAL

The title compound  $C_7H_{11}N_3O_2 \cdot 2HCl$  (AR grade) obtained from Sigma-Aldrich Company was purified by frequent recrystallization process in double distilled water before it was used for growth process. The growth experiment was performed in a constant temperature bath maintained at 32 °C. The salts obtained after recrystallization process were completely dissolved in double distilled water and subjected to continuous stirring using magnetic stirrer for about 6 hours. Once supersaturation of solution is achieved, it was filtered using micro-whatman filter paper to extract any unwanted impurities. The filtered solution was kept in a borosil beaker for further nucleation. The solution was then allowed for constant evaporation at room temperature. In order to sustain constant growth process without fungus formation, few drops of  $H_2O_2$  were added to the above

supersaturated solution. Optically transparent LHMED single crystal of dimensions 14 mm × 6 mm × 3 mm was harvested within a period of a month.

## RESULTS AND DISCUSSION

## Single crystal XRD

Crystal structure and lattice parameters of the as grown  $C_7H_{11}N_3O_2 \cdot 2HCl$  were identified using single crystal X-ray diffraction technique. The crystallographic study has been carried out using Brukeraxs kappa apex2 CCD Diffractometer with  $MoK\alpha$  radiation of wavelength 0.7107 Å at 293(3) K. A tiny crystal of dimensions 0.32 x 0.30 x 0.20 mm<sup>3</sup> was used for experimental analysis. The XRD analysis confirms that the LHMED is crystallized in monoclinic form with space group of  $P2_1$ . The lattice parameters were calculated and the values are  $a=8.21(3)$  Å,  $b=7.11(3)$  Å,  $c=9.51(7)$  Å,  $\alpha=\gamma=90^\circ$  and  $\beta=94.6(5)^\circ$ . The observed values are agreeing well with the reported values [12]. Molecular structure of  $C_7H_{11}N_3O_2 \cdot 2HCl$  is depicted in Fig. 1.

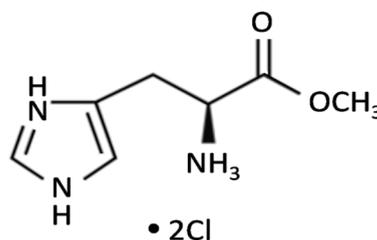


Fig. 1 Molecular structure of  $C_7H_{11}N_3O_2 \cdot 2HCl$

## FT-Raman spectral analysis

FT-Raman spectral analysis has been carried out for the qualitative analysis and identification of compounds. FT-Raman study was performing using BRUKER RFS-27 Raman spectrometer in the frequency range 200–3500  $cm^{-1}$ . Fine crystalline powders of  $C_7H_{11}N_3O_2 \cdot 2HCl$  were used for the spectral analysis. The recorded spectrum of LHMED is depicted in Figures 2. The peak at 3116  $cm^{-1}$  is due to the presence of  $NH_3^+$  group in the crystal. In the spectrum, the aromatic C–H stretching and aliphatic C–H stretching modes are resolved at 3031 and 2889  $cm^{-1}$  [14].

Multiple fine structures at the lower energy modes designate the existence of strong hydrogen bonding interactions of  $NH_3^+$  groups with the  $COO^-$  group. The peak observed at 1756  $cm^{-1}$  indicates the presence of C=O stretching of carbonyl group in the compound. The peak at 1626  $cm^{-1}$  is assigned to C=N stretching of imidazole ring. The aromatic C–C stretching vibration is resolved at 1430  $cm^{-1}$  in the spectrum. The presence of a weak peak at 1279  $cm^{-1}$  is due to C–O stretching vibration of carbonyl group. The peak at 1153  $cm^{-1}$  is due to the stretching vibration of C–O group of ester functionality. In the

lower region of Raman spectrum, the peaks at 989, 854 and 641  $\text{cm}^{-1}$  are due to the ring asymmetric, symmetric stretching and plane deformation. The assignments of various functional groups are detailed in Table 1.

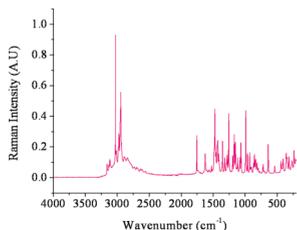


Fig.2. FT-Raman spectrum of  $\text{C}_7\text{H}_{11}\text{N}_3\text{O}_2\cdot 2\text{HCl}$

Table 1 FT-Raman spectral assignments of  $\text{C}_7\text{H}_{11}\text{N}_3\text{O}_2\cdot 2\text{HCl}$

Wavenumber ( $\text{cm}^{-1}$ )	Assignment
3160	$\text{NH}_3^+$ stretching
3031	Aromatic CH stretching
2947	aliphatic $\text{CH}_2$ stretching
2889	Aliphatic C-H stretching
1756	C=O Stretch of carbonyl group
1626	C=N Stretching of imidazole ring
1565	C=O asymmetric stretching
1524	$\text{NH}_3^+$ Symmetric deformation
1473	$\text{CH}_2$ scissoring
1430	C-C Stretching
1414	C=O symmetric stretching
1279	C-O stretching
1257	$\text{CH}_2$ stretching
1153	C-O Stretching of Ester
1081	C-N stretching
989	Ring asymmetric stretching
854	Ring symmetric
836	C-C-O stretch
720	$\text{CH}_2$ rocking
641	Ring deformation
538	Torsional oscillation of $\text{NH}_3^+$

**Optical absorption study**

The property of optical absorption of the title crystal was carried out using the instrument Varian Carry-5E UV-Vis spectrophotometer in the wavelength range between 200 and 1000 nm. So called optical absorption spectrum of the grown crystal is depicted in Fig.3. The LHMED crystal shows almost negligible absorption in the visible and near UV region which facilitate it to be a possible material for nonlinear and optoelectronic applications [15]. The absorption spectrum shows that the transparency of the crystal widen up to the wavelength 228 nm which represents the lower cut-off wavelength or fundamental absorption of the crystal. The low absorption range or wide transparency window between 228 nm and 1000 nm is much suitable for the second harmonic generation of light from the  $\text{C}_7\text{H}_{11}\text{N}_3\text{O}_2\cdot 2\text{HCl}$  crystal.

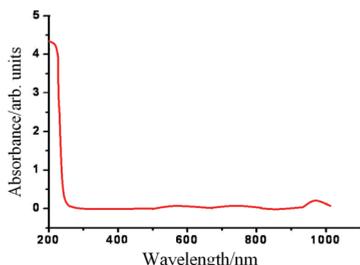


Fig. 3. Optical transmittance spectrum of  $\text{C}_7\text{H}_{11}\text{N}_3\text{O}_2\cdot 2\text{HCl}$  crystal

**Second harmonic generation**

Kurtz and Perry powder technique was followed to find the second harmonic generation of  $\text{C}_7\text{H}_{11}\text{N}_3\text{O}_2\cdot 2\text{HCl}$  crystal [16]. A Q-switched Nd:YAG laser generating the fundamental wavelength 1064nm, pulse width 8 ns having the repetition rate of 10 Hz was used for this purpose. It has been observed that the LHMED sample converts the input radiation of wavelength 1064 nm in to green radiation of wavelength 532 nm. The conversion efficiency of the  $\text{C}_7\text{H}_{11}\text{N}_3\text{O}_2\cdot 2\text{HCl}$  is compared with the microcrystalline KDP sample and it has been observed that

output from the  $\text{C}_7\text{H}_{11}\text{N}_3\text{O}_2\cdot 2\text{HCl}$  sample is 53 mV and for the reference KDP sample is 33 mV.

**Dielectric studies**

The dielectric constant of  $\text{C}_7\text{H}_{11}\text{N}_3\text{O}_2\cdot 2\text{HCl}$  sample was measured in the frequency range from 50 Hz to 5 MHz for the temperature range 313–373 K. The variation of dielectric constant with log frequency at different temperatures is shown in Figure 4. The title compound shows that the dielectric constant is higher at lower frequencies. It is also observed that the dielectric constant decreases exponentially with increasing frequency and reaches a minimum value at higher frequencies. This can be understood on the basis of polarization mechanism. The electronic exchange between ions in the LHMED crystal gives local displacement of electrons in the direction of the applied electric field which gives polarization. In general, dielectric constant of the material is due to the contribution of electronic, ionic, dipolar and space charge polarizations at low frequencies range. As the frequency increases, space charge cannot pursue the external field and hence polarization decreases, giving rise to smaller values of dielectric constant. Also, it has been observed that the dielectric constant decreases with increase in temperatures.

The variation of dielectric loss with log frequency at different temperatures is shown in Figure 5. As the frequency increases, the dielectric loss decreases and at higher frequencies it almost becomes zero. The dielectric constant and dielectric loss show similar responses with frequencies at all temperatures. The low value of dielectric loss at high frequency implies that the crystal possesses better optical quality with lesser defects and this parameter is crucial for NLO materials in their application.

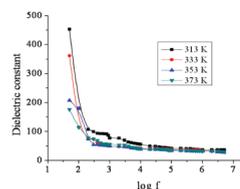


Figure 4 Variation of dielectric constant with log frequency

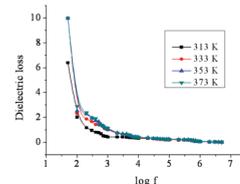


Figure 5 Variation of dielectric loss with log frequency

**AC Conductivity study**

Electrical conductivity is an impurity controlled process in the low temperature region and a defect-controlled process in the high temperature region. The AC conductivity ( $\sigma_{ac}$ ) of the LHMED can be found using the relation  $\sigma_{ac} = 2\pi f \epsilon_0 \epsilon_r \tan \delta$ , where f is the frequency of the alternating current,  $\epsilon_0$  is the permittivity of free space,  $\epsilon_r$  is the dielectric constant and  $\tan \delta$  is the dielectric loss. The variations of AC conductivity with different temperatures for  $\text{C}_7\text{H}_{11}\text{N}_3\text{O}_2\cdot 2\text{HCl}$  samples are shown in the Fig. 6. It has been observed that the magnitude of AC conductivity increases with increase in temperature for the title compound. When the compound is subjected to high temperature, there is a possibility of weakening of the hydrogen bonds and more and more defects are created. This may causes increase in electrical conduction in the sample.

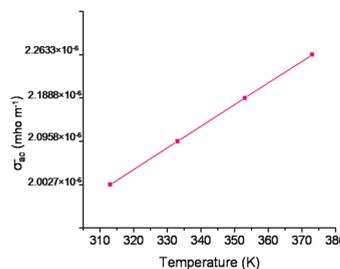
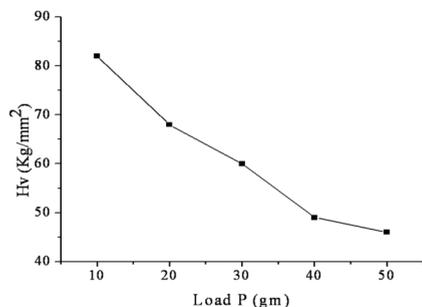


Fig. 6 Variation of AC conductivity with temperature

**MICROHARDNESS STUDY**

Mechanical behaviour of  $C_7H_{11}N_3O_2 \cdot 2HCl$  crystal was analyzed by measuring the microhardness number with different loads. The hardness of an ideal crystal should be independent of the applied load. But in practice, due to normal indentation size effect the load dependence is observed. In present study, static indentations were made on the  $C_7H_{11}N_3O_2 \cdot 2HCl$  crystal for different loads from 10 to 50 g at  $32^\circ C$  with a constant indentation time of 15 s. Due to the formation of possible cracks on the crystal surface at higher loads, the maximum applied load was limited to 50 g. The hardness number  $H_v$  of the grown crystal was calculated using the formula  $H_v = 1.8544 P/d^2$  kg/mm<sup>2</sup> where, P is the applied load in kg and d is average diagonal length of the indentation in mm. A graph is drawn between hardness number ( $H_v$ ) and applied load (P) and is depicted in Figure 7.



**Fig. 7 Variation of hardness number ( $H_v$ ) with applied load (P)**

It has been observed that the hardness of LHMED crystal decreases with increasing load, which is attributed to normal indentation size effect. By employing least square fit method, the value of work hardening coefficient 'n' was estimated from the plot of  $\log P$  versus  $\log d$  (Figure 10). According to Onitsch, for  $1.0 \leq n \leq 1.6$  the material is regarded as hard material and  $n > 1.6$  for soft materials [17]. In the present work, the value of n is calculated as 1.46 and thus confirming that LHMED is a hard material.

**CONCLUSION**

$C_7H_{11}N_3O_2 \cdot 2HCl$  single crystal was grown from aqueous solution by slow solvent evaporation method at room temperature. X-ray diffraction study shows that the  $C_7H_{11}N_3O_2 \cdot 2HCl$  crystal belongs to monoclinic system with the space group  $P2_1$ . Structure  $C_7H_{11}N_3O_2 \cdot 2HCl$  was elucidated by FT-Raman spectroscopy. The optical absorption study shows that the grown crystal is free from any absorption in the UV and visible region and thus confirms the suitability of the crystal for photonic applications. Microhardness study reveals that the hardness number  $H_v$  decreases with increasing load and also LHMED belongs to the category of hard materials. The SHG test reveals that the conversion efficiency of  $C_7H_{11}N_3O_2 \cdot 2HCl$  was observed to be 1.6 times more than that of standard KDP sample. The low value of dielectric constant and dielectric loss combined with the relatively high SHG conversion efficiency make it a capable material for photonic applications.

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