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Crystallization and characterization of nonlinear optical material L-proline monohydrate

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ABSTRACT

L-proline monohydrate an intriguing new organic material for frequency conversion has been grown by slow evaporation solution growth technique at room temperature. Their structural, optical and physicochemical properties were characterized by X-ray powder diffraction, FTIR and FT-Raman spectra. The crystal belongs to orthorhombic system with space group P_{bca} . The mechanical response of the crystal has been studied using Vickers microhardness technique.

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Introduction

In the last decade, organic non-linear optical (NLO) crystals with aromatic rings have attracted much attention because of their high non-linearity, fast response and tailor-made flexibility. The high non-linearity[1-5] makes it possible for organic crystals to double the frequency of GaAlAs diode lasers for generating blue light, which is an important coherent light source. Most of the nonlinear optical materials are currently used in the fabrication of passive and active photonic devices. L-proline is widely employed as a laser frequency doubler and exclusive material of choice for electro-optic modulators. Although the crystal growing technology for these materials is highly developed and their nonlinear optical susceptibilities are sufficient for most of the current photonic applications, they have features that are less than desirable. Hence, new nonlinear optical materials are needed to extend the range of photonic applications. For any device fabrication in the electronic industry pure and defectless single crystals are needed. In this point of view, the L-proline monohydrate single crystal was grown by slow evaporation solution growth method. L-proline monohydrate is a strong amino acid, while mixing it with water it exhibits zwitterionic form. Attempts were made to grow good quality single crystal of L-proline. The grown crystal was subjected to various characterization.

Solubility and Crystal Growth

The low-temperature solution growth technique is widely used for the growth of organic and inorganic single crystals to get more transparent single crystals. The commercially available L-proline (LOBA Chemie) is purified by repeated recrystallization process. The repeated recrystallized materials have been used for growth as charge material [6-14]. Since L-proline is soluble in deionised water, we have chosen deionised water as solvent for our growth. The growth process and the quality of crystals significantly depend on supersaturation. The saturated solution of L-proline was obtained by dissolving the charge material into the solvent with continuous stirring of the

solution using a magnetic stirrer at room temperature (32°C). On reaching saturation, the equilibrium concentration of the solute was determined by gravimetry[15-17]. The beaker containing the solution was optimally closed for controlled evaporation. Transparent bright yellow single crystals were obtained from the mother solution after a week. Fig. 1 shows the Solubility curves of L-proline monohydrate. Fig. 2 shows the as grown crystal of L-proline monohydrate with an optimized solution pH value of 3.5.

Powder X-Ray Diffraction Studies

The structural properties of single crystals of L-Proline Monohydrate have been studied by X-Ray Powder diffraction technique. The X-Ray diffraction studies were carried out using SEIFERT diffractometer with $\text{CuK}\alpha_1$ ($\lambda = 1.5406 \text{ \AA}$) radiation. The powdered samples were scanned over the range $10^\circ - 70^\circ$ at a rate of 1° per minute. From the powdered X-ray data, the various planes of reflections were studied and the lattice parameters were evaluated. The X-ray diffraction pattern is shown in Fig.3. Fig 4 represents the molecular packing of the L-proline monohydrate in the unit cell. It reveals the excellent crystallinity of the grown material. From the studies it is found that the structure of the grown crystal is monoclinic and the crystallographic data is given in Table.1.

FT IR Measurements

The room temperature Fourier transform infrared spectrum[18-22] of L-proline is shown in Fig. 5 was recorded in the region $400-4000\text{cm}^{-1}$ at a resolution of 4cm^{-1} using Perkin Elmer Fourier transform Infrared Spectrophotometer, model SPECTRUM RX1, using KBr pellets containing a fine L-proline monohydrate powder obtained from the grown single crystals, equipped with a LiTaO_3 detector, a KBr beam splitter, He-Ne Laser source and boxcar apodization used for 250 averaged interferogrammes collected for both the sample and the background.

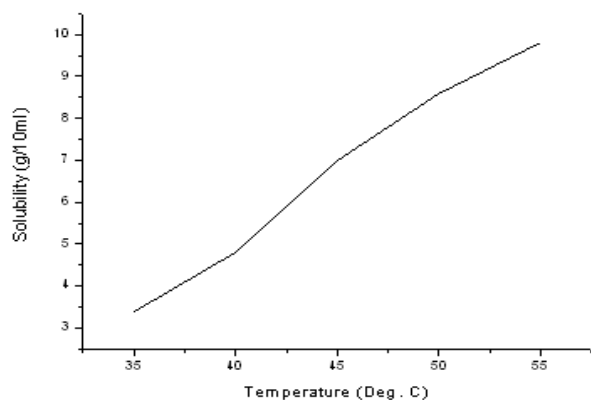


Fig 1. Solubility curves of L-proline monohydrate

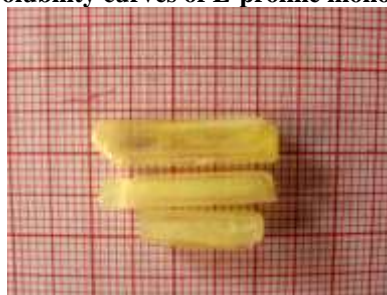


Fig 2. Grown crystal of L-proline monohydrate

Table 1. Crystallographic data of L-Proline Monohydrate

Identification code	LPMH
Empirical formula	$C_5H_{11}NO_3$
Formula weight	133.15
Crystal structure	orthorhombic
Space group	Pbca
Cell parameters	
a (Å)	5.2740
b (Å)	12.0870
c (Å)	20.053
α (°)	90
β (°)	90
γ (°)	90
Volume (Å) ³	1278.3
Z	8
Crystal size	22 x 6 x 2 mm ³

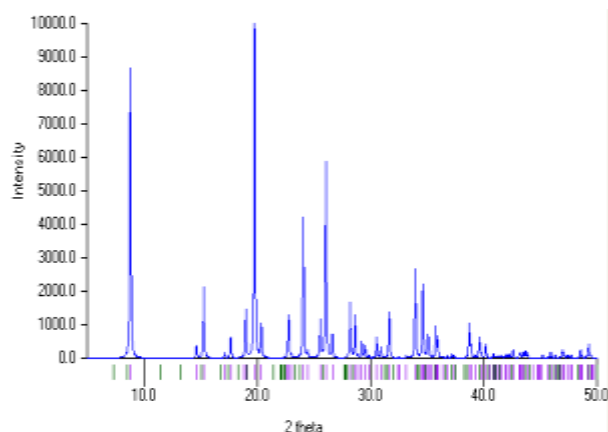


Fig 3. X-ray diffraction pattern of L-Proline Monohydrate

FT Raman Measurements

The FT Raman spectrum was recorded on a BRUKER IFS 66V model interferometer equipped with an FRA-106 FT Raman accessory. The observed spectrum given in Fig. 4.6 was recorded in the 3500 – 100 cm^{-1} Stokes region using the 1064 nm line of a Nd:YAG laser for excitation operating at 200 mW power. The reported wave numbers are believed to be accurate within 1 cm^{-1} . The present vibrational spectroscopic study was carried out with a view of obtaining an insight into the structural

aspects of optical nonlinearity of amino acid based crystals. In order to understand the existence of bonding nature the present study has been undertaken. Thus the molecular structure of the synthesized compound was confirmed by the spectral analysis. The observed wavenumbers, relative intensities obtained from the recorded spectra and the assignments proposed for the title nonlinear optical crystal[23-30] is given in Table. 2. The assignments of bands observed in the vibrational spectrum are an essential step for solving structural and chemical problem. The IR bands observed for the title crystal with their tentative assignments is presented in Table.2.

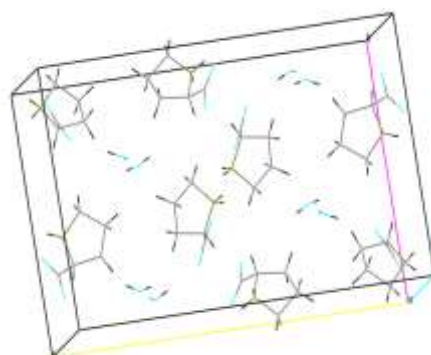


Figure 4. Packing of the L-Proline Monohydrate in the unit cell

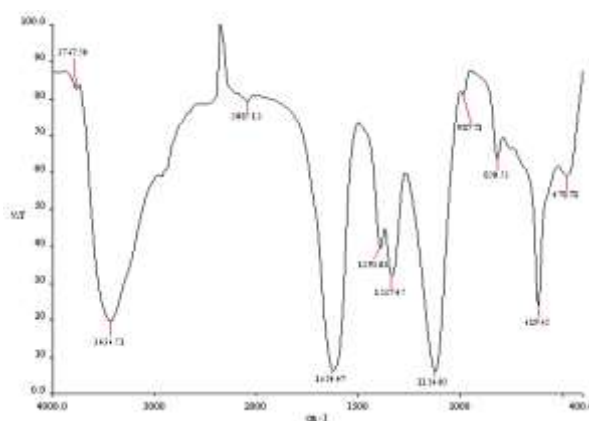


Fig 5. FTIR spectrum of L-proline monohydrate

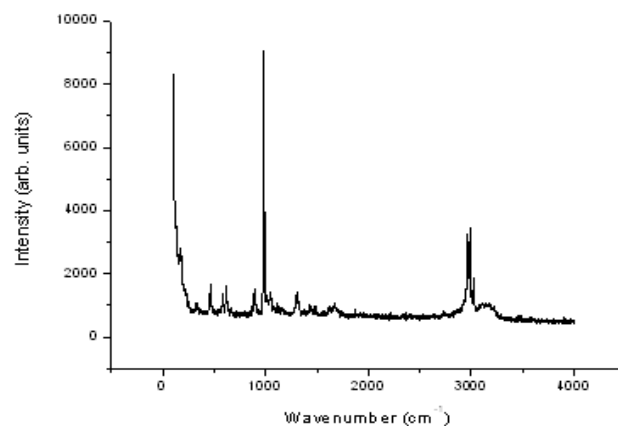


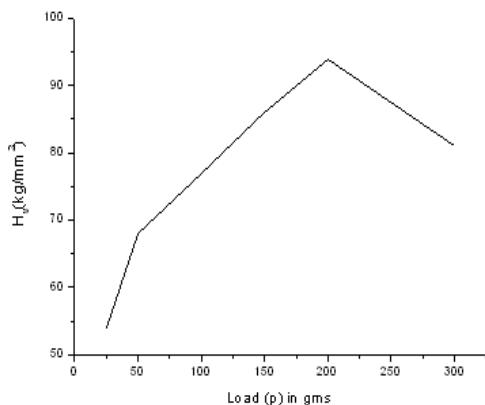
Fig 6. FT-Raman spectrum of L-proline monohydrate

Table 2. Observed IR wavenumber of L-proline monohydrate and its vibrational assignments

Vibrational Assignments		Wavenumber (cm ⁻¹)
FT-IR spectra	FT-Raman Spectra	
3767	-	ν (N-H)
3436	-	vas(NH ₃) ⁺
-	2976	vasCH ₂
2085	-	ν (C-C)
1624	-	ν (C-C)
1393	-	ρCH ₂ , ωCH ₂ , νC-O
1337	-	ωCH ₂ , νC-C, ν(COO) ⁻ , δ _{in} plane C-O-H
-	1266	τCH ₂ , δ _{in} plane(C-H), ρ(NH ₃) ⁺
1124	-	δ _{in} plane(C-H), ρNH ₃ ⁺ , ν(C-C)
987	990	δ _{out} of plane(C-H), ρNH ₃ ⁺
820	-	C-H, CH ₂ out of plane bending
619	610	δ _{in} plane(C-C-C), δ(C-N)
478	466	ρ(COO) ⁻

ν, stretching; ρ, rocking; δ, deformation; ω, torsion;
Hardness Studies

One of the important properties of any device material is its mechanical strength, represented by its hardness. Physically hardness is the resistance offered by a material to localized plastic deformation (moment of dislocations) caused by scratching or by indentation. This resistance is the intrinsic property of the crystal. The hardness is generally measured as the ratio of applied load to the surface area of the indentation. Indentation hardness measurement can, in principle, be carried out at fairly high loads (~ 100 Kg). But for materials which have low hardness and which are available as small- sized sample, it is convenient to make measurements at low loads of < 200g. The low load hardness is called microhardness. The grown crystal with smooth and dominant face was selected for microhardness studies. Indentations were carried out using Vickers indentor for varying loads (25-300 g), for each load, several indentations were made and the average value of diagonal length was used to calculate the microhardness. In ideal circumstances, measured hardness values should be independent of the applied load. But in practice, load dependence is observed. Vickers microhardness number was determined using $H_v = 1.8544 P/d^2$ Kg/mm². The hardness number was found to increase with the load upto 200g and after a load of 200g H_v suddenly decreases as cracks developed in the material. This may be due to the release of internal stresses generated locally by indentation. The plot drawn between the corresponding loads and hardness values of the L-Proline Monohydrate is shown in Fig.7.

**Fig.7. Mechanical behaviour of L-Proline Monohydrate**

Conclusion

Good optical quality L-Proline Monohydrate single crystals were grown by solution growth method at room temperature. It is a promising candidate for NLO applications. The lattice

parameters were found by single crystal XRD technique. The FTIR spectrum and FT-Raman reveals that the confirmation of the molecular structure of the grown specimen. The mechanical properties were examined.

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