

Growth, Structural, Optical and Mechanical analysis of L-Proline Single Crystals

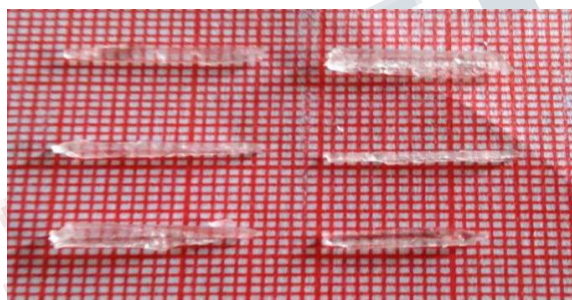
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Abstract:-- Nonlinear optics (NLO) is one of the most attractive fields of current research in view of the applications in the areas such as laser technology, optical communication and data storage technology. The NLO materials will be the key elements for future photonic technologies based on the fact that photons are capable of processing information with the speed of light. Proline is a very important amino acid because of its unique conformation which may affect the structure of proteins, in particular collagen. The present study concentrate on the growth of L-Proline crystal by slow evaporation solution growth technique and its characterization along with its optical properties is reported. The L-proline crystal was harvested after a period of 20 days. The crystal structure of L-proline ($C_5H_9NO_2$) has been determined by X-ray diffraction methods. It crystallizes in the orthorhombic crystal system with space group $P2_12_12_1$, with unit-cell dimensions of $a=11.64$, $b=9.037$, $c=5.260$. The functional groups present in the grown crystal were identified by FT-IR spectral analysis. The transparency range of the crystal was estimated from UV-VIS spectrum. The band gap was found to be 5.8 eV from UV-Visible spectrum. Mechanical property of the grown L-proline crystal was studied by Vickers microhardness tester and the load dependent hardness was measured.

Keywords: L-Proline; slow evaporation technique; XRD; FT-IR; UV-VIS spectrum;



As grown crystals of L-Proline

INTRODUCTION

Nonlinear optical (NLO) materials have shown potential applications in optical information storage, optical logic gates, laser radiation protection, optical communication and optical computing. In earlier days much attention has been paid to organic nonlinear optical materials due to their promising applications in optoelectronics technology. In recent decade, enormous developments have taken place in discovering new NLO materials having large non linear optical coefficients. The important factor for the selection of the materials depends on the physical properties of the crystals and various aspects of applications.

Amino acids are the famous organic materials which can play a vital role in non linear optics as they contain proton donor carboxylic acid (-COOH) group and the proton acceptor amino (NH₂) group. Considerable efforts have been made on the amino acid mixed complex crystals in order to make them suitable for device fabrications. L-Proline is an efficient organic NLO material under the amino acid category. It has a unique structure with the amino group part of the ring structure is important for the shape of Proline. The crystallization and detailed study of Proline reveals its ability for optoelectronic device fabrication. The study and growth of Proline crystal is in the ratio of 1:1 from its salt solution. In the present work, we report the synthesis and single crystal growth of Proline is followed by characterization by powder X-Ray Diffraction, Fourier Transform InfraRed spectral analysis, UV-Vis absorption spectroscopy analysis have been described.

CRYSTAL GROWTH

L-Proline (AR grade) was used for growth as such. L-Proline was taken and dissolved in double distilled water, and stirred continuously for four hours to prepare homogeneous solution. It was filtered using wattman filter paper and the clear filtrate was left undisturbed at room temperature. Slow

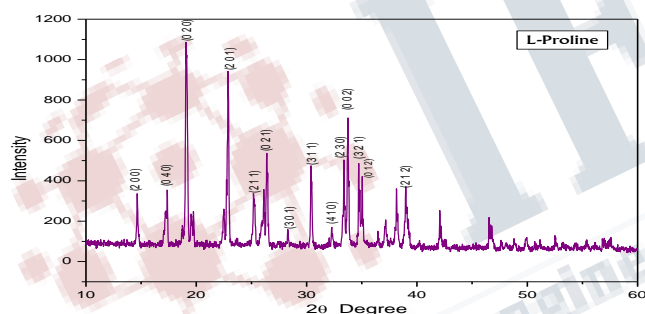
evaporation of the solvent resulted in the formation of transparent crystals after four weeks which were isolated by filtration, washed with little ice cold water and dried in air to get the crystalline product.

CHARACTERIZATION

X-Ray Diffraction Analysis

The powder XRD studies of pure L-Proline crystals were carried out using Analytical XPERT PRO Diffractometer with Cu K α ($\lambda=1.54 \text{ \AA}$) radiation. The samples were scanned for 2θ values from 0° to 80° at a rate of $2^\circ/\text{min}$ at MS University.

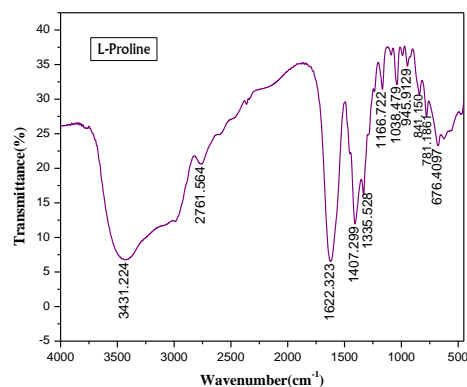
The sharp peaks of XRD pattern indicate high degree of crystalline structure of grown crystal. The observed diffraction pattern has been indexed and miller indices were estimated by Joint Committee on Powder Diffraction Standards (JCPDS) software packages. The observed Powder XRD pattern, the crystallographic data and the lattice parameter values for L-Proline crystals are given in the following graph and tables.



2q	d-spacing [Å]	Hkl
14.6537	6.04516	(2 0 0)
17.3782	5.10309	(0 4 0)
19.0392	4.66146	(0 2 0)
22.8914	3.88500	(2 0 1)
25.2233	3.53088	(2 1 1)
26.3841	3.37810	(0 2 1)
28.2611	3.15786	(3 0 1)
30.3871	2.94160	(3 1 1)
32.2651	2.77455	(4 1 0)
33.3975	2.68302	(2 3 0)
33.7460	2.65610	(0 0 2)
34.7171	2.58400	(3 2 1)
35.0389	2.56100	(0 1 2)

Fourier Transform Infrared Spectroscopic Analysis

The FTIR spectrum identifies the functional groups in the region of frequency $400\text{--}4000 \text{ cm}^{-1}$. The peak at 781.1861 cm^{-1} and 676.4097 cm^{-1} are due to COO^- in plane deformation and COO^- wagging vibration respectively and 1166.722 cm^{-1} is due to O-H in plane bend vibration. The N-H asymmetric stretching is observed at 3431.224 cm^{-1} . Peaks at 1407.299 cm^{-1} and 1335.528 cm^{-1} are attributed to NH_4 bending stretching and CH_2 wagging respectively. The peaks at 1038.479 cm^{-1} , 945.9129 cm^{-1} , 841.1150 cm^{-1} are attributed to the C-N stretching, C-H out of plane deformation, C-C-N symmetric stretching respectively. These values are found to be in good agreement with the reported values of L-Proline. The FTIR spectrum and the complete assignments to the vibrational frequencies of L-Proline crystal are provided in the following graph and table respectively.

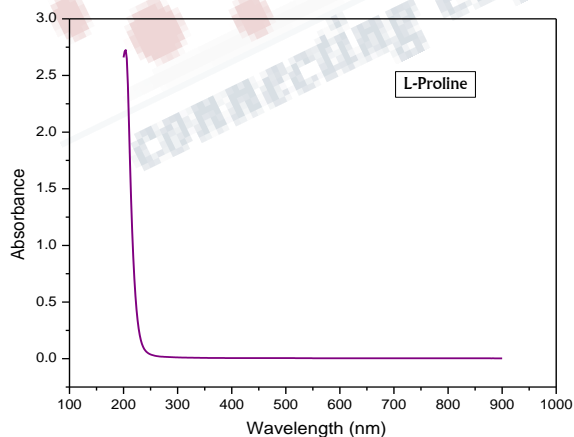
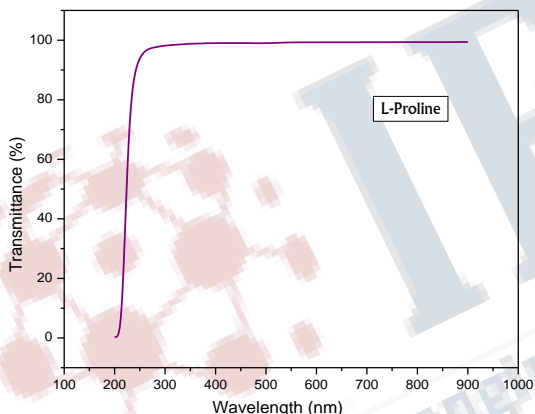


Parameters	L-Proline
a	11.64 Å
b	9.037 Å
c	5.260 Å
V(Å ³)	553.30 Å ³
Structure	Orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
$\alpha = \beta = \gamma$	90°

Wavenumber (cm-1)	Assignment
3431.224	N-H asymmetric stretching
1407.299	NH ₄ bending stretching
1335.528	CH ₂ wagging
1166.722	O-H in plane bend vibration
1038.479	C-N stretching
945.9129	C-H out of plane deformation
841.1150	C-C-N symmetric stretching
781.1861	COO- in plane deformation
676.4097	COO- wagging vibration

UV-Visible Spectroscopic Analysis

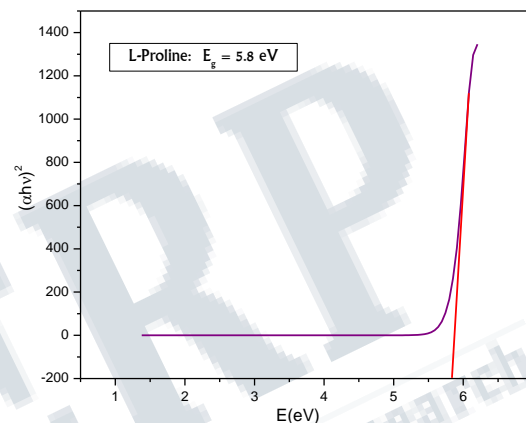
The optical transmission spectra of L-Proline crystals were recorded by UV-VIS spectrophotometer in the range of 200nm-900nm. It is optically transparent with 95% transmission intensity with the low cut-off wavelength at 213nm. The UV-VIS transmittance spectrum and absorption spectrum of L-Proline crystal is given below



The band gap energy (E_g) has been calculated using the Tauc's law,

$$\alpha h\nu = A (E_g - h\nu)^n$$

Where, α is the absorption coefficient, E_g is the band gap energy, $h\nu$ is the incident photon energy and A is a constant dependent on electron and hole effective masses. The n value in above equation depends on whether the material is direct or indirect semiconductor, n is equal to 0.5 for direct transition and equal to 2 for indirect transition. The Tauc's plot for the L-Proline crystals is given below



Forbidden energy band gap of the sample is 5.8 eV

CONCLUSION

In this research work L-Proline organic non linear single crystals have been grown by slow evaporation solution growth technique.

XRD studies for the grown crystals have been carried out and it is found that the L-Proline crystal crystallize in orthorhombic crystal system with the space group of $P2_12_12_1$. The unit cell parameter of the grown L-Proline crystal obtained from the XRD studies are $a= 11.64\text{\AA}$, $b= 9.037\text{\AA}$, $c= 5.260\text{\AA}$, $\alpha = \beta = \gamma = 90^\circ$.

The various functional groups of the grown L-Proline crystals such as COO⁻ in plane deformation, COO⁻ wagging vibration, O-H in plane bend vibration, N-H asymmetric stretching, NH₄ bending stretching, CH₂ wagging, C-N stretching, C-H out of plane deformation, C-C-N symmetric stretching have been identified from FTIR spectra.

Linear optic analysis was done using UV-Visible studies. Forbidden energy band gap of the sample is 5.8 eV. Since the L-Proline crystals were optically active and can be used in production of high efficiency photo voltaic cells and detectors, fabrication of bright long life time light emitting diodes.

The organic nonlinear optical crystals have been used in many applications like information storage and second harmonic generation, photonic device fabrication.

In the future, organic NLO crystals with various ratio and dopants would be grown and characterized by HXRD, UV-Visible spectrometer, Dielectric studies, Micro hardness test, Z-scan impedance, E-DAX, TG/ DTA/DSC, SHG, TH.

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