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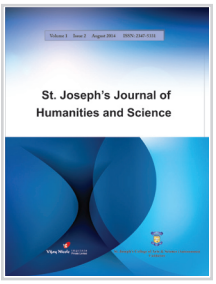

Crystal Growth, Optical and Micro Hardness Studies of an Organic Nonlinear Optical PNDG Single Crystal

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Abstract

Transparent single crystals of PNDG were grown by slow evaporation solution technique to confirm the crystal structure. The grown crystals were subjected to single crystal and it has been studied the structural bands using FTIR spectrum in the region 400-4000cm^{-1}. Optical transmittance of PNDG single crystal has been measured by UV-visible transmittance spectrum. The mechanical strength and work hardening for PNDG crystal is studied using Vicker's micro hardness method and the elastic stiffness is calculated using Wooster's empirical formula.

Keywords: Glycine, β-naphthol, PNDG, UV-Vis Spectrometry, FTIR, Vicker's Microhardness.

Introduction

Non linear optics is a frontier field in science and technology which has found wide applications in the field of telecommunication, optical information, optical storage device etc.,[1&2]. The NLO properties of large organic molecules have been the subject of extensive theoretical and experimental investigations. Among organic crystals for NLO applications, amino acids display specific features of interest such as (i) molecular chirality, which secures acentric crystallographic structure, (ii) absence of strongly conjugated bonds, leading to wide transparency ranges in the visible and UV spectral regions, (iii) zwitterionic nature of the molecule, which favors crystal hardness [3-5]. Glycine is the simplest of all amino acids and is known to crystallize in three different polymorphs: α, β, and γ [6,7]. In the present study we have reported about the growth aspects of PNDG single crystals by slow evaporation method. Here the glycine transforms into α-phase on heating. The α-glycine has the space group. In the solid state,α-glycine contains a deprotonated carboxylic acid group(COO^-) and protonated amino acid group(NH_3^+). This dipolar nature combined with centrosymmetric point group makes PNDG an ideal candidate for NLO application. The grown crystals have been subjected into FTIR, UV-Visible and Micro Hardness studies.

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Experimental Procedure

The saturated solution was prepared using commercially available glycine (CH2 NH2 COOH) and β-naphthol. Glycine and β-naphthol was dissolved in a 100 ml beaker using water and dmso as the solvent. The solution was stirred well for about six hours at room temperature and the saturated solution was filtered with Whatman (Grade No.1) filter paper in clean vessel. The vessels containing the solutions were covered with perforated polythene sheets and kept at dust free atmosphere. The solution was allowed for slow evaporation. Crystals with (1.1 mm * 0.8 mm) was harvested and then subjected to characterization studies.

Results and Discussion

FTIR Spectral Analysis

The infrared spectroscopy is effectively used to identify the functional groups of the samples. Fourier transform infrared (FTIR) was recorded in the range 400-4000cm^{-1} using the Perkin Elmer grating infrared spectrophotometer. The recorded Fourier transform infra-red (FT-IR) spectrum of PNDG crystal is shown in Figure 1.

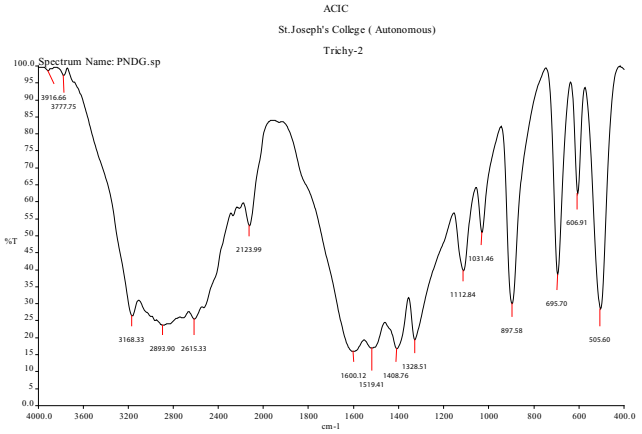

Figure 1: FTIR Spectrum of PNDG Crystal

In the FT-IR spectrum the peak observed at 3168 cm^{-1} are assigned to NH_3^+ stretching vibration. The peak observed at 2893cm^{-1} is attributed to C-H group. The peak observed at 2615cm^{-1} is contributed to NH_3^+ stretching vibration. The combinational bond observed from the spectrum is very strong (2123 cm^{-1}) compared to α-glycine (2121 cm^{-1}). The peak observed at 1600cm^{-1} is due to asymmetric CO_2 stretching. The peak observed at 1519cm^{-1} is assigned to NH_3^+. The peak observed at 1408 cm^{-1} correspond to COO^- symmetric stretching. The peak observed at 1328cm^{-1} are attributed to CH_2 twisting. The peak observed at 1112cm^{-1} is due to NH_3^+rocking.The peak observed at 1031cm^{-1}are assigned to CCN asymmetric stretching vibration. The peak observed at 897cm^{-1} is contributed to CCN symmetric stretching vibration. The peak observed at 695cm^{-1} corresponds to COO^- bending. The peak observed at 606cm^{-1} is due to COO^- wagging. The peak observed at 505 cm^{-1} is assigned to COO^- rocking.

It is concluded that from the FTIR data comparison, the observed functional group of the grown PNDG single crystal are in good agreement with the literature value [8] of α-Glycine and they are presented in the table 1.

Table 1: Comparison of FTIR Spectrum of PNDG Crystal with α-Glycine

PURE GLYCINE	PNDG	α- GLYCINE (Literature value)	TENTATIVE ASSIGNMENT
893	897(S)	898	ν_s (CCN)
910	1031(VS)	1030	ν_s (CCN)
1033	1112(S)	1109	$\rho(NH_3^+)$
1133	1328(S)	1328	$\tau(CH_2)$
1333	1408(M)	1409	ν_s (COO^-)
1413	1519(W)	1513	(NH_3^+)
-	1600(W)	1609	ν_{as} (CO_2)
-	2123(S)	2121	Combinational Bond
-	3168(S)	3169	$\nu(NH_3^+)$
-			

τ – Twisting , ρ – Rocking , δ – Bending , ω – Wagging, – Stretching, S - Strong , VS – Very Strong , W – Weak, M – Medium

UV-Visible Spectral Analysis

The UV-Vis spectrum gives limited information about the structure of the molecule because the absorption of UV and visible light involves promotion of the electrons in the σ and π orbital from the ground state to a higher energy state. To find the transmission range optical transmission spectrum of the PNDG was recorded. The recorded transmission and absorption spectra are shown in the figure 2&3. The transmission was found at 318nm and the absorption SPR peak was found at 192nm. The crystal is found to be transparent in the visible and near

IR region,an essential parameter required for frequency doubling process[9]. This is the advantage of the use of amino acids where the absence of strongly conjugated bonds leads to the wider transparency ranges in the visible and UV spectral regions[10]. The lower cut off at 200nm combined with the very good transparency window makes the material suitable for optoelectronic applications.

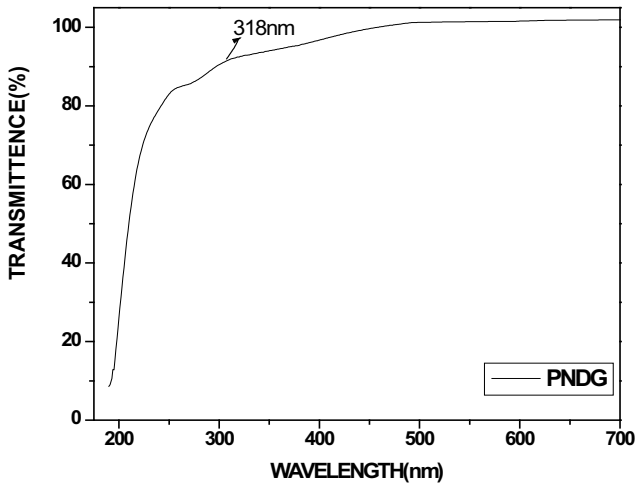

Figure 2: UV-Vis Transmittance Spectrum of PNDG Crystal

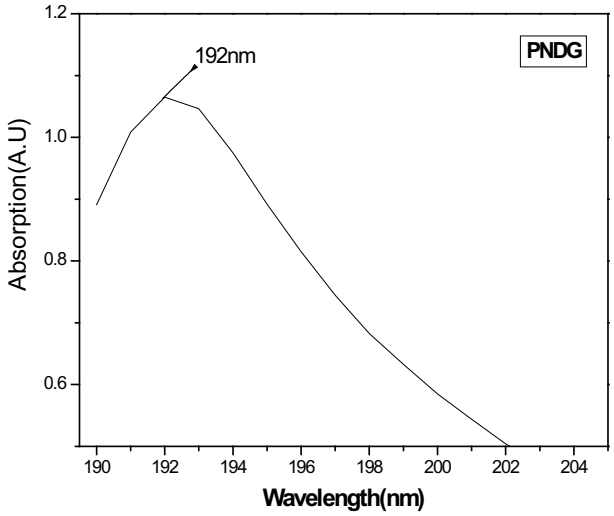

Figure 3: UV-Vis Absorption Spectrum of PNDG Crystal

Micro Hardness Analysis

The hardness of a material is a measure of its resistance to plastic deformation. Microhardness studies are carried out using MHT-10 microhardness tester (Anton-Paar) for PNDG crystals to determine its hardness. Load of different magnitudes as 25gm, 50 gm, 100 gm were applied. The indentation time was fixed as 10 s for each trial. Repeated trials were performed to ascertain the correctness of the observed results.

The Vickers microhardness number (H_V) was calculated using the equation [11,12] given as follows:

$$H_V = 1.8544\ P/d^2\ (kg/mm^2) \quad (1)$$

Where P is the indenter load (kg) and d is the diagonal length of the impression (mm) and 1.8544 is a constant of a geometrical factor for the diamond pyramid. Figure 3 shows that the hardness of the grown PNDG single crystal increases with increase in load. Using Meyers law we calculate the Meyer's index (n) to analyse the nature of the material. The size of intentation and load are related through Meyer's law[13-15],

$$P = k_1 d^n \quad (2)$$

From the slope of log P vs log d shown in figure 4 gives the estimated n value. In the present study the obtained n value of PNDG crystal is 3.6 and we find that the material belongs to the soft material category. Since the value of n is larger than 2, the hardness of the material increases with increase of load conforming the prediction of Onitsch[16].According to Hays-Kendall's approach load dependent hardness may be expressed by,

$$P = W + A_1 d^2 \quad (3)$$

$$H_0 = 1854\ A_1 \quad (4)$$

Where W is the minimum load initiate plastic deformation.A_1 is the load independent constant,H_0 is the corrected hardness. The value of W and A_1 can be calculated by plotting the graph between P and d^2. The estimated value of W and A_1 from the plot drawn between P and d^2 is shown in the figure 5. The value of W and H_0 for various loads are given in the table 5.3. Also the elastic stiffness constant is calculated using Wooster's empirical formula [17], which is given by

$$C_{11} = (Hv)^{7/4} \quad (5)$$

The Hardness Parametrs of PNDG crystal for various loads is also given in table 2.

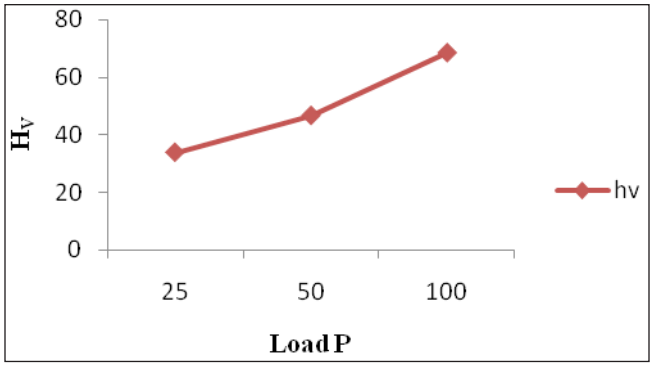

Figure 4: Graph Between Applied Load ρ and Vickers Micro Hardness Number

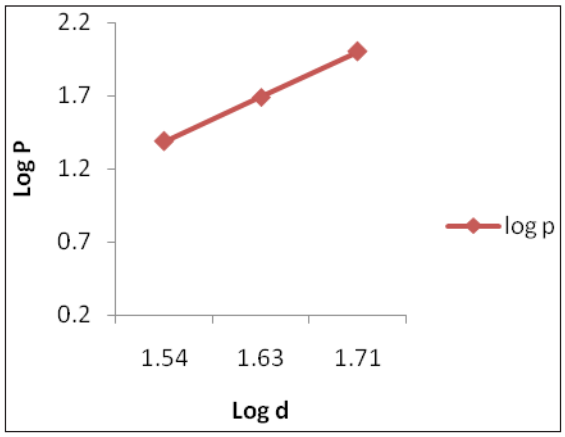

Figure 5: Graph Between Log d and Log ρ

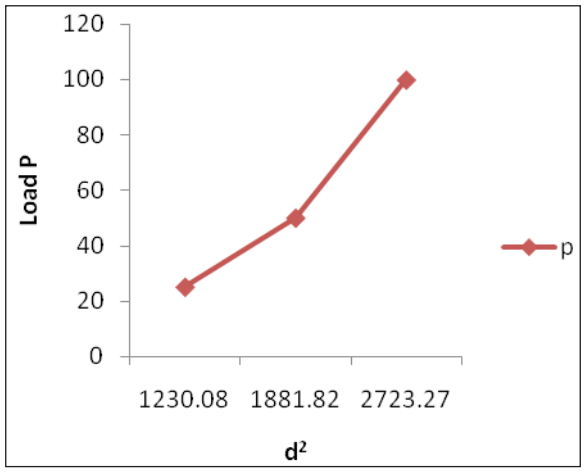

Figure 6: Graph Between d^2 and Applied Load ρ

Table 2: Hardness Parameters of PNDG Crystal

Load(P)	N	H_V	A_1	W	H_0	$C_{11}*10^{14}$pa
25	3.6	35.75	0.05	-36.504	92.72	5.2267
50	3.6	46.55	0.05	-44.091	92.72	8.2958
100	3.6	68.35	0.05	-36.164	92.72	16.2477

Conclusion

Good quality transparent single crystals of PNDG have been grown by slow evaporation technique at room temperature. From the FTIR spectrum ,the observed functional group of the grown PNDG single crystal are in good agreement with the literature value of α-glycine and a very strong bond is observed at 1031cm^{-1} due to symmetric CNN stretching. UV-Vis spectra shows that the grown PNDG single crystal has a good transmission window in the visible region suitable for NLO application and the lower cut of frequency wavelength is192 nm. Vickers Microhardness study on the PNDG single crystal reveals that the H_V and C_{11} increases with increase in load.

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