

Experimental Studies on L-Phenylalanine L-Phenylalaninium Benzoic Acid

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ABSTRACT

L-Phenylalanine L-Phenylalaninium Benzoic Acid (LPB) was successfully grown from aqueous solution by slow evaporation method. The grown crystal was characterized using powder x-ray analysis, Optical absorption (UV-vis-NIR), Fourier Transform Infrared (FT-IR), Fourier Transform Raman (FT-Raman) spectral studies, and DTA/TGA studies.

Keywords: LPB, XRD, FT- IR & FT-Raman, TGA

I. INTRODUCTION

The importance of amino acids in nonlinear optical (NLO) applications is due to the fact that all the amino acids have chiral symmetry and crystallize in noncentrosymmetric space groups [1]. In the solid state, many amino acids contain a deprotonated carboxylic acid group (COO) and protonated amino group NH₃⁺. This dipolar nature leads to peculiar physical and chemical properties in amino acids, thus making them ideal candidates for NLO application. Among them, L-phenylalanine is an essential protein amino acid, which is used by the body to build neurotransmitters [2]. Phenylalanine, an essential amino acid commonly found in proteins, plays a key role in the formation of variety of physiologically important chemicals that transmit signals between nerve cells besides possessing excellent NLO properties.

II. EXPERIMENTAL DETAILS

L-phenylalanine and benzoic acid taken in 1:1 ratio were dissolved in double distilled water to prepare the

aqueous solution of LPB. In deionized water, L-phenylalanine and benzoic acid undergo the following chemical reaction to produce LPB.



Synthesized salt of LPB was obtained from the solution by evaporating the solvent and collecting the precipitate formed at the bottom of the container.

The solubility of the synthesized material of LPB was carried out in deionized water by gravimetric method [3] at various temperatures. The recrystallized salt of LPB was used to prepare the mother solution at room temperature by continuous stirring. The beaker was kept in a constant temperature bath. After attaining the saturation, the equilibrium of the solute was analysed gravimetrically. The experiment was repeated for different temperatures (30, 35, 40, 45 and 50 °C). The solubility curve of LPB is shown in Figure 1.

Based on the solubility data the solution was prepared at room temperature for growth experiments. Single crystals of LPB were grown from their aqueous

solution using slow solvent evaporation technique. The solvent of the supersaturated solution was allowed to evaporate through the perforated lid of the container. Due to spontaneous nucleation optically clear tiny crystals were formed in a period of 5-7 days. The defect free and well-shaped ones were chosen and used as seed crystals for further growth experiments. Good optical grade and colorless crystal of dimension upto $11 \times 7 \times 6 \text{ mm}^3$ was grown over a period of 35-40 days

by using slow evaporation technique. The photograph of as grown LPB single crystals is shown in Figure 2.

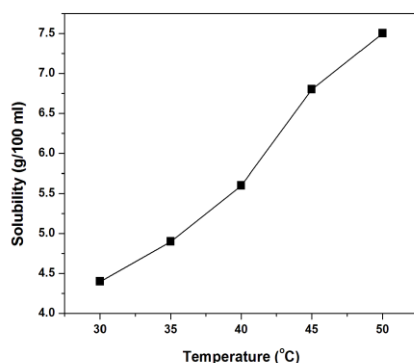


Figure.1. The Solubility curve of LPB



Figure 2. Photograph of as grown LPB single crystal

III. RESULTS AND DISCUSSION

3.1 X-ray diffraction analysis

The structural property of LPB was studied by Single crystal X-ray diffraction technique. Single crystal X-

ray diffraction studies of LPB crystal was carried out, using BRUKER NONIUS CAD4/MAC4 X-ray diffractometer with $\text{Cu K}\alpha$ radiation. From the single crystal analysis it was observed that the crystal belongs to monoclinic crystal system having non-centrosymmetry with P2_1 space group. The summary of key crystallographic information is given in Table 1. The powder XRD pattern of the grown LPB crystal is shown figure 3.

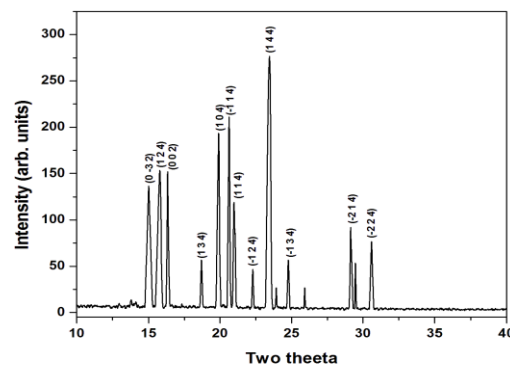


Figure.3. Powder XRD spectrum of LPB crystal

3.2 FT-IR and FT-Raman Analysis

The FT-IR spectrum of LPB was recorded using BRUKER IFS-66V spectrometer in the range between 4000 and 500 cm^{-1} and is shown in Figure 4. The FT-Raman spectrum of LPB is plotted in the range 0 to 4000 cm^{-1} and is shown in Figure 5.

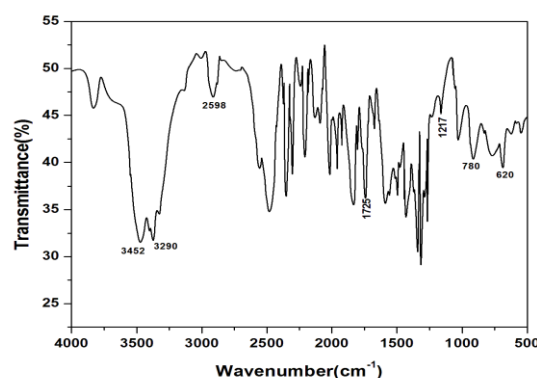


Figure 4. FT-IR Spectrum of LPB

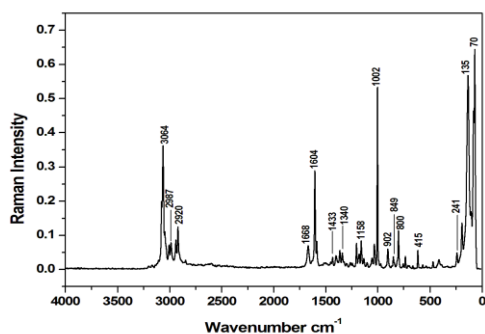


Figure 5. Experimental FT-Raman Spectrum of LPB

Table 1

S.NO	Frequency		Vibrational Assignments
	FT-IR	FT-Raman	
1.	3452	-	ν NH ₂
2.	3290	-	γ NH ₃ ⁺
3.	-	3077	ν CH
4.	-	3046	γ NH ₃ ⁺
5.	-	2987	γ CH ₃
6.	2960	-	ν CH ₂
7.	1725	-	ν CC
8.	-	1668	ν C=N
9.	1598	1585	δ CH ₂
10.	1504		δ HCC
11.	1480		CH δ
12.	-	1433	δ HCC
13.	1417	-	δ OC ₃
14.	-	1400	CH ₃ def
15.	-	1364	CH ₃ def
16.	-	1262	γ CHOH
17.	1217	-	ν CC
18.	-	1178	ω CH ₃
19.	-	1158	δ HCC
20.	-	1132	ν C-C
21.	-	1101	ν CH
22.	-	1054	δ CH
23.	-	1032	ν OC
24.	-	1002	δ CCC
25.	-	902	CH def

26.	-	850	γ CCCC γ NCCC	+
27.	-	800	δ ONO + δ CCC	
28.	780	-	γ CN	
29.	-	734	γ CN	
30.	620	-	δ CCC	
31.	-	617	γ CCCC	
32.	-	-	γ CCCC	
33.	555	571	δ CN	
34.	-	471	β C-C	
35.	-	135	ν C-C	
36.	-	105	τ CCOC	

ν -stretching ; δ -in-plane bending; β -bending; τ -torsion; **def**- deformation; ω - wagging

The broad envelope between 3400 and 2500 cm⁻¹ includes absorption of stretching bands due to NH₃⁺ ion of the amino acid. The NH₃⁺ asymmetric and symmetric stretching vibrations are positioned at 3290 and 2598 cm⁻¹ respectively.

Multiple fine structures at the lower energy mode of the envelope indicates the strong hydrogen bonding interaction of NH₃⁺ group with weak absorptions of COO⁻ group at 1598 and 1417 cm⁻¹. The presence of L-phenylalanine ions in the crystal structure is reflected in the band of the NH₂ rocking (780 cm⁻¹).

The O-H group gives rise to three vibrations (stretching, in-plane bending and out-of-plane bending vibrations). The O-H group vibrations are likely to be the most sensitive to the environment, so they show pronounced shifts in the spectra of the hydrogen bonded species. The hydroxyl stretching vibrations are generally observed in the region around 3500 cm⁻¹ [4]. In the case of the un-substituted phenols it has been shown that the frequency of O-H stretching vibration in the gas phase is 3657 cm⁻¹ [5]. Similarly in our case a very strong FT-IR band at 3452 cm⁻¹ is assigned to O-H stretching vibrations. The

hydrogen bonding effect through hydroxyl group leads to dimer conformation OH stretching mode calculated at 3404.35 cm^{-1} .

The assignments of methyl group vibration make a significant contribution to the title molecule spectra. The presence of C–H vibrations ensures that the place of methyl group in benzene ring. The asymmetric and symmetric C–H vibrations for methyl group usually occur in the region between 2975 and 2920 cm^{-1} [6].

Strong carbonyl absorption at 1725 cm^{-1} identifies the COOH and COO[−] groups of the compound. For the title compound, the theoretical C=O stretching band is observed at 1725 cm^{-1} and 1758 cm^{-1} . Further strong band observed at about 1217 cm^{-1} is due to C–COO[−] stretching. The presence of L-phenylalanine ions in the crystal structure is reflected in the bands of the COO[−] wagging (555 cm^{-1}). The detailed vibrational assignments of fundamental modes of LPB along with the FT-IR, FT-Raman experimental frequencies and their spectral assignments are shown in Table 1.

3.3 Optical absorption spectrum

The optical properties of a material provide information on the electronic band structures, localized states and types of optical transitions. Figure 6 shows the optical absorption spectrum of LPB. The good absorption property of the crystal in the entire visible region suggests its suitability for second harmonic generation. From the spectrum it is observed that the UV cut-off wavelength lays around 250 nm . The lower cutoff wavelength around 250 nm is due to the π – π^* transition in this compound. Using Tauc's relation (Tauc 1974), a graph has been plotted to estimate the band gap value. Figure 7 shows the plot of $(\alpha h\nu)^2$ versus $h\nu$, where α is the optical absorption coefficient and $h\nu$ is the energy of the incident photon. The energy gap (E_g) is determined by extrapolating the straight line portion of the curve to $(\alpha h\nu)^2 = 0$ and E_g is found to be 4.92 eV . Thus

confirming the wide band nature of aminoacid based optical materials [7].

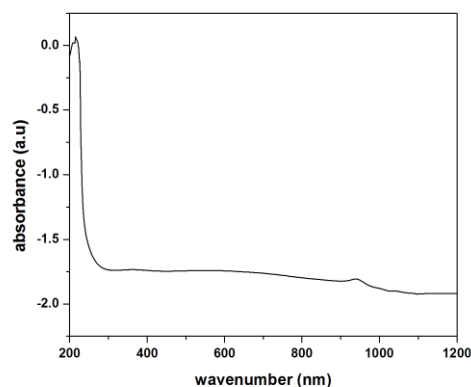


Figure 6. Optical absorption spectrum of LPB crystal

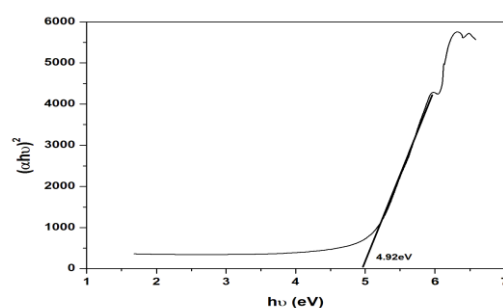


Figure.7. Optical band gap of LPB crystal

3.4 Thermogravimetric analysis

The thermal stability of L-phenylalanine-benzoic acid (LPB) single crystal was estimated by TGA and DTA techniques. Thermo gravimetric (TG) and differential thermal analyses (DTA) for LPB were carried out by NETZSCH STA 409C thermal analyzer. The TGA and DTA traces are shown in Figure 8. TGA curve shows three stages. In the DTA curve the endothermic peak at $119\text{ }^{\circ}\text{C}$ is due to melting of the sample, which is also observed in TG curve. The first stage occur in the temperature range of $116 - 163\text{ }^{\circ}\text{C}$ with a weight loss of 28% , and the second stage occurs in the temperature range $163 - 287\text{ }^{\circ}\text{C}$ with a weight loss of 20% . The slope from 163 to $287\text{ }^{\circ}\text{C}$ in the TGA trace is due to the weight loss which may be attributed to liberation of ammonia molecule. In the successive third stage, there is a weight loss of 17% between 287 and $402\text{ }^{\circ}\text{C}$, which is assigned to the

decomposition of carboxylic group. Finally residue is observed. Based on the results of TGA and DTA, the maximum temperature for NLO application of this crystal is limited to 116 °C.

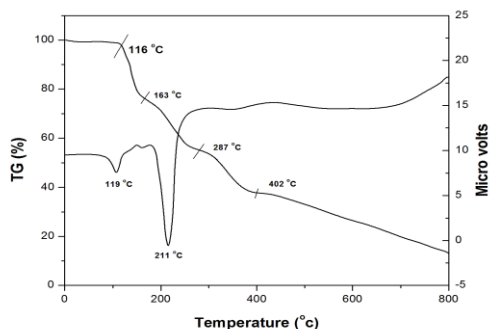


Figure 8. TGA and DTA curve of LPB crystal

IV. CONCLUSION

Optically good quality single crystals of LPB were grown by slow solvent evaporation technique. The crystalline nature of grown crystal is confirmed by single crystal X-ray diffraction analysis and it is found that the crystal belongs to the monoclinic system with $P2_1$ space group. Spectral assignments are carried out for various vibrational frequencies. Optical absorption spectrum was recorded for the given crystal and it is found that it has minimum absorption between 250 - 1200 nm. The optical band gap of the material is found as 4.92 eV. Thermal stability of the LPB crystal was found to be three stages of weight loss.

V. REFERENCES

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