Synthesis and characterization of L-Phenylalaninium trichloroacetate hemihydrate (PACAH) single crystals

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Single crystals of L-Phenylalaninium Trichloroacetate Hemihydrate (PACAH) [$C_9H_{12}NO_2^+$.$C_2Cl_3O_2^-$.1/2H_2O], which is semi-organic in nature and showing non-linear optical property have been grown by slow evaporation solution technique at room temperature. Solubility of the material for different temperatures has been determined. The grown crystals have been subjected to various characterization studies such as X-ray diffraction, CHNS, FTIR analysis, UV-Vis spectrum, TGA/DTA, powder SHG test, laser damage threshold, dielectric and microhardness studies.

(Received April 15, 2011; accepted after reviewing May 31, 2011)

Keywords: Crystal growth, X-ray diffraction, Thermal expansion, Nonlinear optics, Dielectric response

1. Introduction

In the past few decades, the design and characterization study of inorganic, organic and semi-organic second-order nonlinear optical (NLO) and ferroelectric materials has become a hotspot for a lot of physics and chemistry scholars due to their potential applications in advanced laser technology and optoelectronics applications. It is well known that the deliberate selection of reaction reagents is crucial to produce more efficient multifunctional materials of good quality. The key factors for material selection depend not only on laser conditions but also on the physical properties of the crystals such as transparency, damage threshold and thermal stability [1-2]. Semi-organic crystals have been proposed as a new approach for materials with interesting nonlinear optical properties [3]. L-Phenylalanine is an essential aromatic and hydrophobic amino acid commonly found in proteins and plays vital role in the formation of variety of physiologically important chemicals that transmit signals between nerve cells. It helps to improve memory and learning. To our best knowledge, a few single crystals of L-Phenylalanine used as a NLO material have been reported [4-7]. L-Phenylalaninium Trichloroacetate Hemihydrate (PACAH) which crystallizes in noncentrosymmetric space group C2 has been reported previously [8]. In the present work, an attempt has been made to grow single crystals of PACAH by slow evaporation solution technique. Optical, thermal, electrical and mechanical properties of PACAH crystals have been investigated. The second harmonic generation (SHG) in the crystal has been confirmed by the Kurtz powder technique and the efficiency of frequency doubling has been estimated.

2. Experimental

2.1 Synthesis

PACAH was synthesized from L-Phenylalanine and trichloroacetic acid (AR grade). L-Phenylalanine and trichloroacetic acid were dissolved in millipore water (18.2 MΩ cm^{-1}) in the molar ratio of 1:1. The prepared solution was stirred well for 3 hours using a magnetic stirrer at room temperature and pH was adjusted to 2. The solution was taken in a covered container and kept at room temperature. After 10 days the PACAH material crystallized at the bottom of the container. The material was three times recrystallized for purification and used for solubility studies and crystal growth. Good-quality highly transparent PACAH single crystals of size 16 x 4 x 2 mm^3 were obtained in 20 days and shown in Fig. 1.

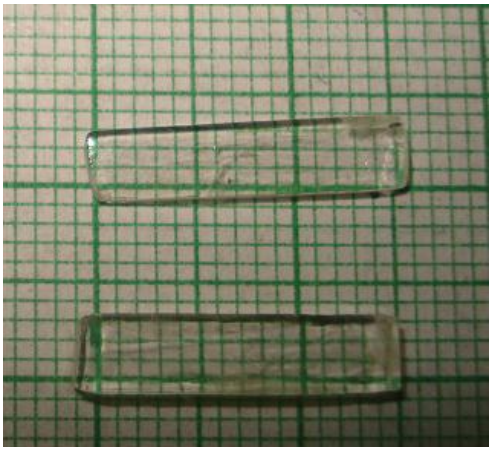

Fig. 1. As grown crystal of PACAH.

2.2 Solubility

The solubility of PACAH in water was determined for five different temperatures such as 30, 35, 40, 45 and 50ºC. The solubility was determined by dissolving the three times recrystallized solute in Millipore water (high purity water) in an airtight container maintained at a constant temperature with continuous stirring to reach the equilibrium in 6 hours. After attaining the saturation, the equilibrium concentration of the solute was analyzed gravimetrically. The solubility curve obtained was shown in Fig. 2. PACAH has a positive gradient of solubility.

The solubility of PACAH = $a + bT + cT^2$ where a = 3, b = 1.65 and c = .006

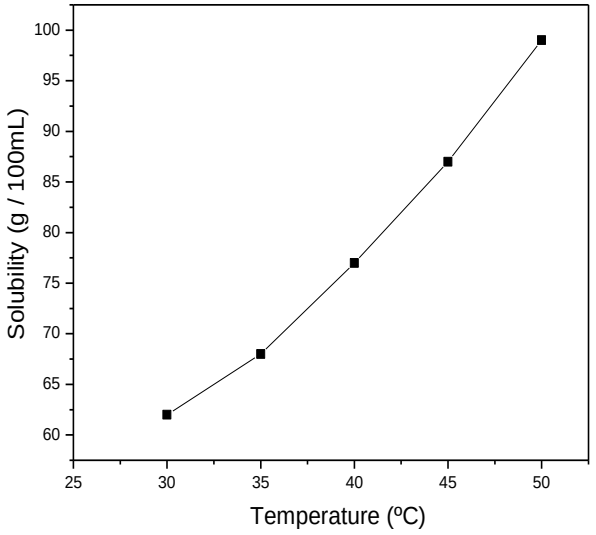

Fig. 2. The solubility studies of PACAH crystal.

3. Results and discussion

3.1 X-ray diffraction analysis

Single crystal X-ray diffraction study was carried out using ENRAF NONIUS FR 590 single crystal diffractometer to determine the lattice parameter values. The unit cell dimensions are a = 19.78 Å, b = 6.16 Å, c = 26.66 Å, β = 109.52°, V = 3060 $Å^3$ and it belongs to monoclinic system with space group C2. Further the grown crystals were characterized by X-ray powder diffraction using an automated analytical MPD model diffractometer using CuKα radiation of wavelength λ=1.5406 Å to verify the correctness of lattice parameter values. Finely crushed powder of PACAH crystal was subjected to powder X-ray diffraction analysis. The sample was scanned over the range $10^0 – 70^0$ at a rate of 1° $min.^{-1}$ and the prominent peaks were indexed. The recorded X-ray pattern of PACAH is shown in figure 3. The lattice parameters derived are in good agreement with the reported values confirming the identity of the grown crystal [8] and are given in Table 1.

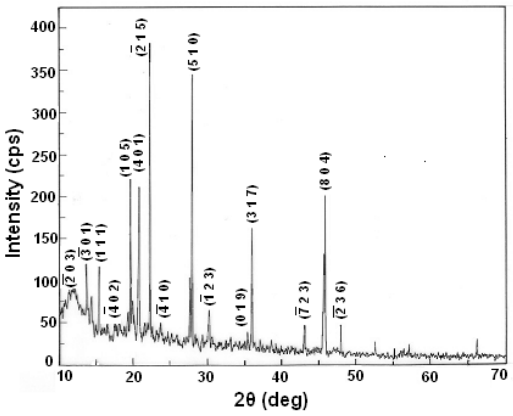

Fig. 3. Powder X-ray diffraction of PACAH crystal.

Table 1. Lattice parameters of PACAH crystal.

Lattice Parameters	Literature [8]	Present work [powder XRD]	Present work [single XRD]
a (Å)	19.67	19.68	19.78
b (Å)	6.11	6.31	6.16
c (Å)	26.58	26.39	26.66
β (deg)	109.6	109.3	109.52

3.2 CHN analysis

The chemical composition of the synthesized material PACAH was determined by carbon, hydrogen and nitrogen (CHN) analysis using Elementar Vario EL III-GERMANY analyzer. The weight percentages of carbon, hydrogen and nitrogen present in PACAH sample along with the theoretically calculated values are given in Table 2. The calculated values agree well with the experimental values. The coordination of half water molecule with L-Phenylalaninium Trichloroacetate is further supported by the TG analysis, which shows weight loss in the first dehydration step corresponding to half water molecule and the synthesized PACAH material has been quantitatively confirmed.

Table 2. Chemical analysis of PACAH.

Empirical formula: $C_9H_{12}NO_2^+ .C_2Cl_3O_2^- .1/2H_2O$
Molecular weight: 337.57

Element	Composition (%)	
	Experimental	Theoretical
Carbon	41.40	39.13
Hydrogen	3.75	3.88
Nitrogen	3.98	4.15

3.3 Fourier transform infrared analysis

For the spectroscopic study, FTIR spectrum was recorded using Bruker IFS-66 FTIR spectrometer in the range 4000-450 cm^{-1} at room temperature. The FTIR spectral analysis of PACAH was carried out by KBr pellet technique in order to identify the functional groups present in PACAH crystals. The recorded FTIR spectrum of PACAH shown in Fig. 4 is compared with the standard spectra of the functional groups [4, 9-12]. The absorption peak at 3419 cm^{-1} is assigned to OH group in the water molecule. The peak at 3031 cm^{-1} is due to the presence of CH group in PACAH. The peaks at 1958 cm^{-1}, 1138 cm^{-1} and 1099 cm^{-1} are assigned to the presence of C=C stretching. The intense peaks at 1745 cm^{-1} and 1512 cm^{-1} establish the presence of C=O stretching. NH_3^+ asymmetric stretching vibrations produce its peak at 1666 cm^{-1}. Phenyl quadratic ring stretching produces its characteristic peak at 1590 cm^{-1}. The presence of phenyl sextant ring stretching is clearly illustrated by the intense peak at 1326 cm^{-1}. The peak at 1288 cm^{-1} is assigned to the presence of CH_2 wagging. The absorption peak at 1073 cm^{-1} establishes the presence of benzene ring. The intense peak at 832 cm^{-1} reveals the presence of CCl_3 stretching. The absorption peak at 574 cm^{-1} reveals the presence of wagging vibration of COOH. Thus the presence of all the functional groups occurring in PACAH is identified. The absorptions of PACAH have been compared with those of parent compound L-Phenylalanine [4] and the shifts in the positions of the characteristic peaks confirm the formation of the new compound. The observed vibrational frequencies and their assignments are listed in Table 3.

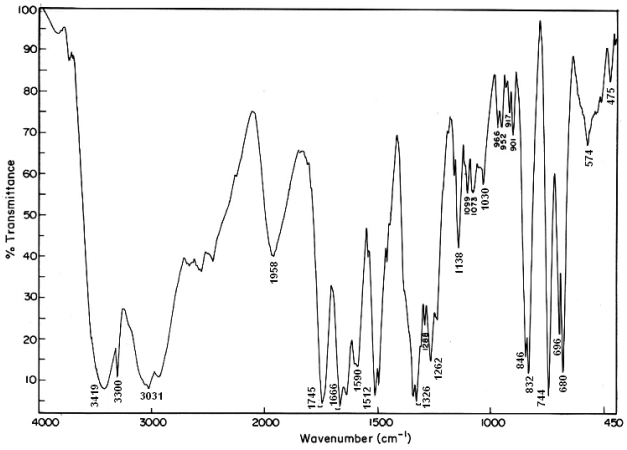

Fig. 4. FTIR spectrum of PACAH crystal.

Table 3. FTIR Frequency assignment for PACAH.

Observed FTIR frequencies (cm^{-1})			Corresponding assignment
PACAH(Present work)	L-Phenylalanine Nitric acid [5]	L-Phenylalanine [4]	
3031	3082	3028	C-H Stretching
1958, 1138 and 1099	1125 and 1095	1957	C=C stretching
1745 and 1512	1510	1596	C=O stretching
1288	1209	-	CH_2 wagging
1073	1075	1081	Presence of benzene ring
832	-	-	CCl_3 stretching
574	-	-	wagging vibration of COOH

3.4 UV-Vis –NIR analysis

Optical window transparency width is an important characteristic of an NLO material. Optical absorption spectrum was recorded for the grown crystals in the region 200-2000 nm by varian 5E UV-Vis-NIR spectrophotometer. A graph of absorbance vs wavelength ignoring the loss due to reflection is shown in Fig. 5. In the UV, visible and near-IR regions, the material is found to be transparent. It is observed that the lower cut off wavelength is about 220 nm. From the fundamental absorption peak at 220 nm, it is calculated that the band gap energy of PACAH crystal is 5.6 eV. The absence of absorption in the range between 220 nm and 1350 nm shows that this crystal might be used for optical window applications and harmonic generation.

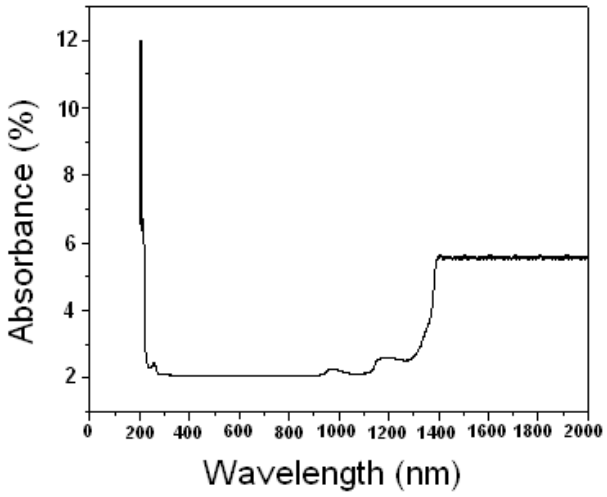

Fig. 5. UV-Vis-NIR spectrum of PACAH crystal.

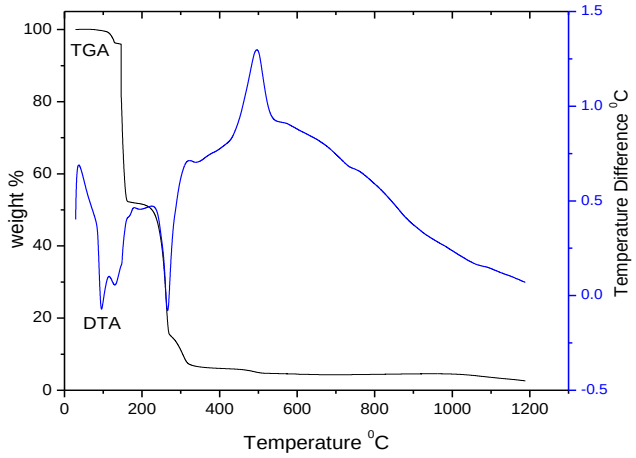

Fig. 6. TG/DTA curve of PACAH crystal.

3.5 Thermal analysis

Thermal analysis was performed on the grown crystals to study the thermal stability and melting point. The melting point determined using the capillary tube method was 96°C [13]. Thermogravimetric analysis was carried out for the as grown crystals of PACAH using Netzsch STA 409 analyzer in the temperature range 30°C to 1200°C in the nitrogen atmosphere at a heating rate of 10 K/min. The TG/DTA spectrum is shown in Fig. 6. The TG spectrum reveals that the weight loss occurs in three steps. The weight loss between 118°C and 134°C is consistent with the weight of half molecule of water crystallization present in the crystal. Second weight loss is observed between 231.80°C and 272.51°C with weight loss of 38.1%. These weight losses are associated with sharp endothermic peaks in DTA spectrum indicating the absorption of heat energy for decomposition. Further increase in temperature doesn't produce any significant peaks and a residue of 2.599% remains. The DTA curve shows an endothermic peak in the absence of any weight loss in TGA at 96.83°C indicating the melting point of the crystal. Hence, thermal studies reveal that the crystal can be stable up to 96.83 °C

3.6 NLO activity

The most widely used technique for initial screening of materials for second harmonic generation is the Kurtz powder technique [14]. Powder SHG measurement was carried out for PACAH using the Kurtz and Perry technique with 1064 nm laser radiation. A Quanta ray of Nd-YAG laser producing pulses with a width of 10 ns and a repetition rate of 10 Hz was used. The powder sample of PACAH was tightly packed in the micro-capillary tubes of uniform diameter (1.5 mm). The input laser energy incident on the capillary tube was chosen as 2.4 mJ/pulse. The SHG was confirmed by the emission of green radiation (532 nm) and the optical signal was collected by a photomultiplier tube (PMT). The optical signal incident on the PMT was converted into voltage output at the CRO. The PACAH showed a powder SHG efficiency of 0.51 times that of standard NLO material, KDP. Comparison of nonlinear optical properties of title compound with other competing materials is shown in Table 4.

Table 4. Comparison of nonlinear optical properties of L-Phenylalanine compounds with KDP equaling 1.0.

Compound	Cut off wavelength (nm)	SHG efficiency in comparison with KDP	Thermal stability °C
PACAH (Present work)	220	0.51	96.83
L-phenylalanine nitric acid [5]	295	0.26	205
L-phenylalanine L-phenylalaninium Perchlorate [6,7]	237	1.4	272

3.7 Laser – induced damage threshold studies

One of the important properties in the choice of a material for nonlinear optical applications is its optical damage tolerance. Because of the high optical intensities involved in nonlinear processes, the nonlinear materials must be able to withstand high power intensities [15]. In the present study, an actively Q-switched diode array side

pumped Nd-YAG laser was used for the laser damage threshold (LDT) studies. The pulse width and the repetition rate of the laser pulses were 10 ns and 10 Hz respectively at 1064 nm radiation. For this measurement, the laser beam was focused onto the sample using a lens with focal length of 20.5 cm. A well polished sample with a clean surface was taken for this present study. Laser damage threshold studies were made on the grown PACAH bulk crystals. The damage threshold is found to be 3.9 GW/cm^2 which is low while comparing with L-Phenylalanine L-phenylalaninium perchlorate (LPAPCl) crystal (7.4 GW/cm^2) [7] and high while comparing with KDP (200 mW/cm^2) [16].

3.8 Dielectric studies

Semi-organic materials are attractive for electro-optic and ferroelectric applications because of their fast switching response and hence the dielectric properties of the grown crystal have been studied. The dielectric study on PACAH single crystal was carried out at room temperature using the instrument, HIOCKI 3532-50 LCR HITESTER (42 Hz – 5 MHz). A sample dimension of 8.69 x 4.55 x 2.05 mm^3 having silver coating on the opposite faces was placed between the two copper electrodes and thus a parallel plate capacitor was formed and the dielectric constant of the sample was measured at room temperature. The variation of dielectric constant and dielectric loss with frequency at room temperature is shown in figure 7. It is found that the dielectric constant has high values in the lower frequency region and then it decreases with an increase in frequency. It is observed that the dielectric loss also reduces at higher frequencies. The characteristic of low dielectric loss at higher frequency ranges shows that the specimen possesses good quality with less defects which is important for NLO applications

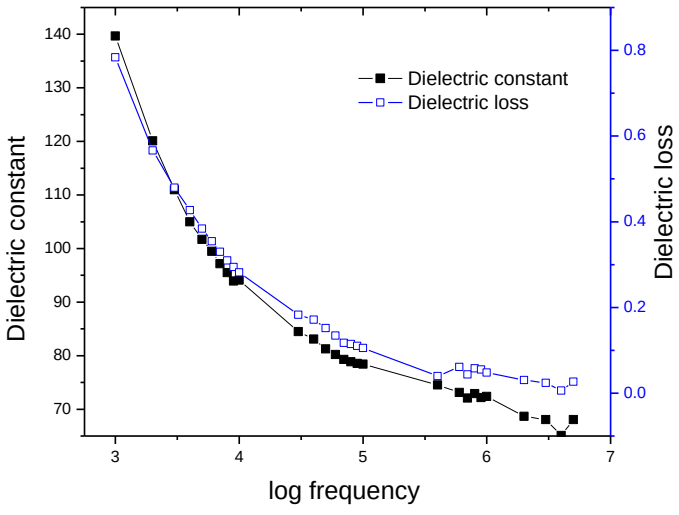

Fig. 7. Permittivity and losses of PACAH at room temperature.

3.9 Microhardness analysis

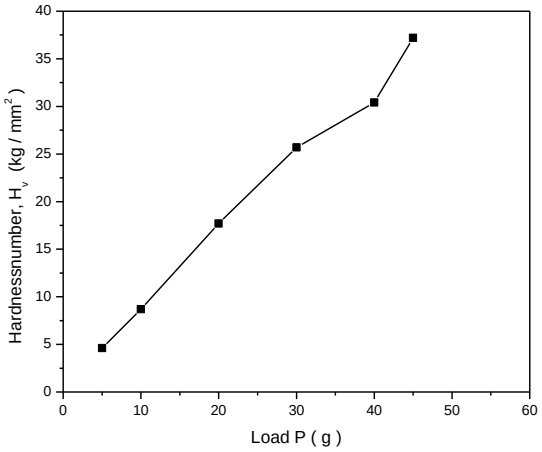

Fig. 8. Hardness Number (H_v) vs Load (P).

The structure and composition of the crystalline solids are inviolably related to the mechanical hardness. Microhardness testing is one of the best methods of understanding the mechanical properties of materials such as fracture behavior, yield strength and brittleness index [17-18]. The Vicker's hardness measurement was carried out on the grown crystals to assess the mechanical behavior of the material using REICHERT MD 4000E Ultra microhardness tester fitted with a Vicker's diamond pyramidal indenter attached to a REICHERT POLYVAR 2 MET microscope. The static indentations were made on the crystal by varying the load from 1 to 50 g at room temperature with a constant indentation time of 10 s. The Vickers microhardness number H_v of the crystal is calculated using the relation $H_v = 1.8544\ P/d^2$ kg/mm^2, here, H_v is the Vickers hardness number in kg/mm^2, P is the applied load in kg and d is average diagonal length of the indentation in mm. A graph plotted between hardness number (H_v) and applied load (P) is shown in figure 8. The maximum value of hardness for PACAH crystal at room temperature is found to be 37.2 kg/mm^2 for the load of 50 g. Beyond the load of 50 g, significant cracking occurs, which may be due to the release of internal stresses generated locally by indentation.

4. Conclusion

Semi-organic single crystals of PACAH was grown by slow solvent evaporation technique. The solubility of PACAH for water at various temperatures has been determined. X-Ray diffraction studies confirm the monoclinic structure and noncentrosymmetric space group of the grown crystals at room temperature. Chemical composition of the synthesized material was confirmed by CHNS analysis. Various functional groups present in the grown crystal were identified by FTIR spectroscopy. The UV-Vis-NIR analysis shows that there is no absorption in the range between 220 nm and 1350 nm thus confirming the suitability of material for optical window applications.

It is evident from the thermal studies that the crystal is thermally stable up to 96.83°C. The powder SHG efficiency of this PACAH crystal is 0.51 times that of KDP. The damage threshold is 3.9 GW/ cm^{-2}. The variation of dielectric constant and dielectric loss were studied with varying frequency at room temperature. The Vicker's hardness number of PACAH was found to be 37.2 kg/mm^2. Thus, good optical property and significant SHG efficiency make PACAH crystal, a potential material for the fabrication of photonic devices.

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