Growth and characterization of novel semiorganic nonlinear optical crystals of L-phenylalanine hydrochloride (LPHCl)

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ABSTRACT
Semiorganic nonlinear optical (NLO) material, L-phenylalanine hydrochloride (LPHCl) single crystals of dimension $42 \times 8 \times 6 \text{ mm}^3$ have been grown by slow evaporation technique, and are reported for the first time. The grown crystal was confirmed by single crystal X-ray diffraction and FT-IR analysis. Optical absorption spectrum shows very low absorption in the entire visible region and the cut-off wavelength is occurs at 350 nm. The optical energy gap is found to be 3.7 eV. The optical behaviour of the grown crystal was analyzed by PL study. The second harmonic generation of the grown crystal was confirmed by Kurtz and Perry powder technique. TG/DTG analyses confirm the two stages of decomposition in the sample and it further proves the relatively high thermal stability (229°C) of the crystal in comparison to other NLO crystals of amino acid family. The frequency dependent dielectric properties of the crystal were studied for different temperatures.

Keywords: A1. X-ray diffraction, A2. Growth from solution, B1. Nonlinear optical material.

INTRODUCTION
Materials with large second order optical nonlinearities find wide applications in the field of laser technology, laser communication, data storage technology and optoelectronic technologies [1-3]. Recently semiorganic crystals have been proposed as new candidates with interesting nonlinear optical properties as they possess high thermal and mechanical stability compared to organics [4, 5]. Amino acids are favorable materials for NLO applications as
they contain a proton donor carboxyl acid (COOH) group and proton acceptor amine (NH$_2$) group. They are naturally occurring chiral species; crystallize in noncentrosymmetric space groups, which is an essential criterion for nonlinear optical (NLO) applications [6]. There has been considerable progress in the amino acid family crystals like L-histidine perchlorate, L-arginine tetrafluoroborate, L-arginine fluoride are some of the semi organic materials proved promising for their applications in the field of NLO [7-9]. L-phenylalanine is an essential protein amino acid, which is used by the body to build neurotransmitters [10]. A thorough scan of literature reveals that X-ray diffraction, neutron diffraction and ESR studies have already been reported [11-13]. In the present work, a systematic investigation has been carried out on L-phenylalanine hydrochloride (LPHCl) single crystals by slow evaporation solution growth technique. The crystal is characterized by single crystal X-ray diffraction, UV-Vis-NIR and FT-IR analysis. The grown crystal was also subjected to thermal, dielectric, photoconductivity, photoluminescence and second harmonic generation test and these properties have been investigated and reported for the first time to the best of our knowledge.

MATERIALS AND METHODS

Synthesis and crystal growth
The starting materials for synthesis were of AR grade and used as purchased. L-phenylalanine and hydrochloric acid were taken in 1:1 stoichiometric ratio. The amount of L-phenylalanine salt was calculated and dissolved in deionized water for an hour to for complete dissolution. Then the appropriate amount of HCl was added to the solution. The resultant solution was continuously stirred for three to four hours. The chemical reaction is as follows:

$$\text{C}_9\text{H}_{11}\text{NO}_2 + \text{HCl} \rightarrow \text{C}_9\text{H}_{12}\text{NO}_2\text{Cl}$$

The solution was allowed to evaporate at room temperature. Optically transparent single crystal of dimension 42 × 8 × 6 mm$^3$ was obtained in a period of 25 days. Fig. 1 shows the photograph of as grown single crystal of LPHCl.

![Fig. 1. Photograph of as grown LPHCl single crystal](image)

Characterization
The grown crystal of LPHCl was confirmed by single crystal X-ray diffraction analysis. Single crystal XRD data was collected by ENRAF NONIUS CAD4 single crystal X-ray diffractometer with MoK$_\alpha$ ($\lambda=0.71073$ Å) radiation. The FTIR spectrum was recorded using BRUKER IFS 66V FT-IR spectrometer with KBr pellet technique for the range 4000 – 400 cm$^{-1}$. The optical absorption studies have been carried out using a VARIAN CARY 5E UV-
Vis-NIR spectrophotometer in the range of 200 – 2000 nm. The thermal behaviour of the grown crystal was investigated using SDT Q600 thermal analyzer. Sample of weight 4.555 mg was heated in a crucible between 20 to 700°C at a heating rate of 20°C min⁻¹ in nitrogen atmosphere. The frequency dependent dielectric constant and dielectric loss of LPHCl were measured using HIOKI 3532-50 LCR HI-TESTER for various temperatures (308, 328 and 348 K). A sample of dimension 5 x 2 x 1 mm³ having silver coating on the opposite faces was placed between the two copper electrodes to form a parallel plate capacitor. The capacitance of the sample was noted for the applied frequency (100 Hz to 5 MHz). The photoluminescence (PL) spectrum was recorded for the crystal using JOBIN YUVIN spectrometer. The excitation wavelength used for the present study is 325 nm. The surface morphology of the grown crystal is investigated using a JEOL/EO-JSM-5610 Scanning Electron Microscopy. The photoconductivity studies on the LPHCl single crystal were carried out by connecting it in series with DC power supply and a picoammeter (Keithley 485) at room temperature. Kurtz and Perry SHG test was used to find the NLO efficiency of the grown crystal [14].

RESULTS AND DISCUSSION

Single crystal X - ray diffraction study
It is inferred from the X-ray diffraction study that LPHCl belongs to orthorhombic system with non-centrosymmetric space group P2₁2₁2₁. The cell parameters are a = 27.762(6) Å, b = 7.039(1) Å, c = 5.376(4) Å and V = 1050 Å³. The data obtained in the present work matches well with the literature [11].

![FTIR spectrum of LPHCl crystal](image)

FTIR analysis
The Fourier transform infrared (FT-IR) spectrum of LPHCl is shown in Fig. 2. From the spectrum it is observed that the very broad peaks at 3430 and 3026 cm⁻¹ indicate the presence of N-H stretching and C-H stretching respectively. The peak appearing at 1732 cm⁻¹ is due to C=O stretching. A sharp peak at 1478 cm⁻¹ corresponds to COO⁻ stretching. A small sharp
peak at 1357 cm\(^{-1}\) is due to OH bond. The peaks at 1127, 1098 and 1954 cm\(^{-1}\) confirm the presence of C=C stretching and the C=N stretching is at 1047 cm\(^{-1}\).

**Optical absorption study**

Fig. 3 represents the optical absorption spectrum of LPHCl. The UV cut-off wavelength of the sample is found to be at 350 nm and the absorption is very less in the entire visible region and part of IR region. The optical band gap is obtained by plotting the graph between \(h\nu\) versus \((\alpha h\nu)^2\) (Fig. 4). From the graph, the optical energy gap of LPHCl is determined as 3.7 eV.

**Second harmonic generation**

The second harmonic generation (SHG) test on the LPHCl crystal is performed by Kurtz and Perry powder SHG method. The fundamental beam of Nd: YAG laser with 1064 nm wavelength, pulse duration of 8 ns and 10 Hz repetition rate is focused onto the powdered sample of LPHCl and KDP. When the input pulse of 3.2 mJ is passed through the sample and KDP, the output signal of 55 and 112 mV are obtained from LPHCL and KDP respectively. Thus the NLO efficiency of LPHCL is two times to that of KDP crystal.

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E_g = 3.7 \text{ eV}
\]
Thermal studies
TG-DTG traces of L-phenylalanine hydrochloride is shown in Fig. 5. It is observed from the thermogram that there are two stages of weight loss. During the first stage of decomposition, there is a major weight loss of 59.42% at 250°C, which is assigned to the decomposition of the compound Benzeneethanamine, which is present in the LPHCl. In the successive stage there is a weight loss of 40.61% between 343 and 368°C, due to the decomposition of carboxylic group. Finally no residue is observed.

The DTA trace of LPHCl is shown in Fig. 6. It illustrates a major endotherm starting at 229°C. It is coinciding with the first stage of decomposition. As there is no other endotherm below 229°C, the compound is seen to decompose without melting. Hence the material can be applied for NLO up to 229°C. The thermal analysis of LPHCl show that it is thermally more stable (229°C) when compared with other semiorganic analogs such as LADI (145°C), LADP (173.9°C), LAF (200°C) of amino acid family [15-17].

![Fig. 5. TG/DTA thermogram of LPHCl crystal](image)

![Fig. 6. DTA thermogram of LPHCl crystal](image)
Dielectric studies

Fig. 7 shows the plot of dielectric constant ($\varepsilon_r$) versus log frequency for 308, 328 and 348 K. It is seen that the value of dielectric constant is high in the lower frequency region for all the temperatures and then it decreases with increase in frequency up to 10 kHz. The high value of dielectric constant at low frequency region is attributed to space charge polarization due to charged lattice defects [18]. Beyond 10 kHz, it is almost constant and is saturated at higher frequencies. A graph is drawn between dielectric loss and log frequency for various temperatures (308, 328 and 348 K) and is shown in Fig. 8. The low value of dielectric loss at high frequency suggests that the grown crystals possess good optical quality. This parameter is of vital importance for nonlinear optical materials in their applications [19].

Photoluminescence studies

The Photoluminescence of LPHCl crystal provides information of different energy states available between valence band and conduction band responsible for radiative recombination. Fig. 9 represents the PL spectrum of LPHCl single crystal. The experimental result shows that there are two emissions of the sample at 404 and 650 nm. When the sample is excited with 325 nm, absorption of the sample is observed between 360 and 370 nm. Due to this absorption, the emission of K-violet is observed at 404 nm. After this emission a small absorption is also observed around 410nm which may be due to the affinity between NH$_3^+$ and Cl$^-$ ions present in the grown crystal. This absorption leads to an emission of H$_\alpha$ red around 650 nm.

Fig. 7. Variation of dielectric constant with frequency

Fig. 8. Variation of dielectric loss with frequency
**Photoconductivity studies**

Fig. 10 shows the plot of dark current and photo current against electric field. It is observed from the graph that both dark current and photo current increase linearly with the applied electric field, but the photo current is less than the dark current which is termed as negative photoconductivity. The negative photoconductivity in a solid is due to the reduction in the number of charge carriers or their life time in the presence of radiation [20]. The decrease in mobile charge carriers during negative photoconductivity can be explained by the stockman model [21].

**CONCLUSION**

Single crystals of L-Phenylalanine hydrochloride are grown by slow solvent evaporation technique in a period of 25 days. The structure of the grown crystal was confirmed by single crystal XRD analysis. FT-IR spectrum confirms the various functional groups present in the grown crystal. Optical absorption study reveals the absorption edge at 350 nm. Thermal studies reveal that the crystal is thermally stable up to 229 ºC. The SHG efficiency is found to be nearly two times higher than KDP. Owing to its transparency, thermal stability and non-centrosymmetric crystal structure, LPHCl can be used as promising material for NLO and photonic device applications.
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REFERENCES