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## Growth, Structural and Optical Behaviour of L-Histidinium perchlorate: A Nonlinear Optical Single Crystal

R. Vincent Femilaa<sup>1</sup>, M. Victor Antony Raj<sup>1</sup>, J. Madhavan<sup>1, a</sup>

<sup>1</sup> – Department of Physics, Loyola College, Chennai, India

a – [jmadhavan@gmail.com](mailto:jmadhavan@gmail.com)



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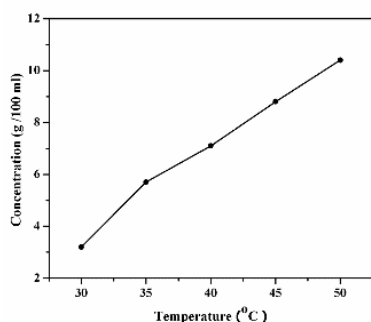
**Keywords:** NLO, LHPCL, XRD, DFT, HOMO, LUMO, KDP.

**ABSTRACT.** In this work, a non linear optical (NLO) material L-Histidinium Perchlorate (LHPCL) was reported for both the experimental and theoretical study, where the title compound, which is a single crystal was grown using a slow evaporation method at the room temperature and from the single crystal analysis, the crystal was observed to be a monoclinic crystal which had non-centrosymmetry with space group  $P2_1$ . From Powder XRD study, both the experimental and theoretical XRD patterns were found to be similar in comparison. From density functional theoretical (DFT) computations, the optimization of the molecular structure and the corresponding vibrational harmonic frequencies were calculated for the title compound and to evaluate the energetic behaviour of the material the HOMO and LUMO orbital energy gaps were performed. The NLO test was performed and a second harmonic efficiency was found nearly to be 3.44 times that of KDP.

**Introduction.** Large number of L-histidine compounds had excellent nonlinear optical property [1]. By combining a counter inorganic ion and an organic ion, a typical semi-organic crystal was formed. Amino acids and inorganic acids were good raw material for the production of semi-organic crystal [2]. To synthesize new organic materials with large second-order optical nonlinearities, many investigations were conducted in order to satisfy day-to-day technological requirements. In telecommunications, optical computing, optical data storage, etc they had an innumerable potential applications. Due to inherent ultra fast response, the large optical susceptibilities and high optical thresholds for laser power was compared to inorganic materials and the organic nonlinear materials attracted a great deal of attention [3]. In the present work an attempt was made to grow a NLO material L-Histidinium Perchlorate (LHPCL) using slow evaporation method with L-Histidine and Perchloric acid. Then the material was characterized and the results were reported from the characterization techniques such as XRD, DFT and HOMO-LUMO.

**Experimental Procedure.** A stoichiometric amount of L-Histidine (Merck-99%) and high purity perchloric acid (Merck) was added in deionized water to achieve the synthesis of the title compound LHPCL and the solubility (g LHPCL / 100ml  $H_2O$ ) of LHPCL was measured [4]. Fig 1 shows the study of variation of solubility with temperature and its corresponding curve. After a period of 45 days, crystals of dimension up to 6mm x 5mm x 2mm were obtained. The crystals were free from visible inclusions and highly transparent. The photograph of as grown crystal of LHPCL was shown in Fig 2.

Using ENRAF NONIUS CAD 4 single crystal X-ray diffractometer with  $MoK\alpha$  radiation ( $\lambda=0.71073$  Å), the grown crystal was subjected to single crystal X-ray diffraction study at room temperature. The crystal was observed to be a monoclinic crystal from the single crystal analysis and had non-centrosymmetry with space group  $P2_1$ . Table 1 shows the crystal and its structural refinement data.



*Fig. 1. Solubility curve of LHPCL.*

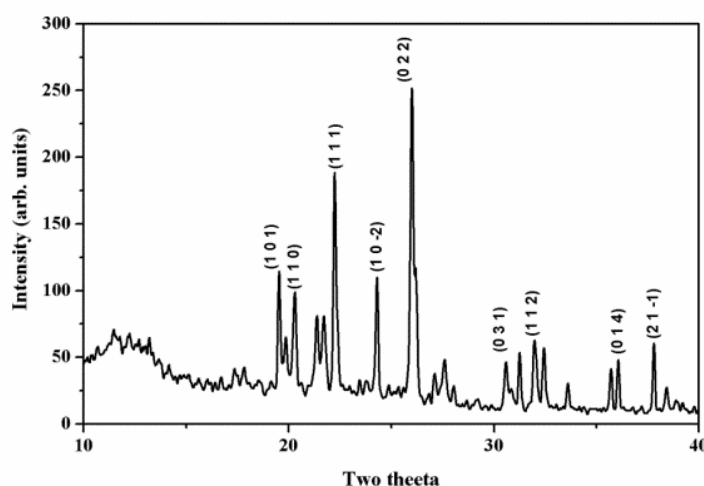


*Fig. 2. Photograph of grown LHPCL single crystal.*

*Table 1. Crystal parameters of LHPCL.*

Empirical Formula	$\text{ClO}_6\text{C}_6\text{N}_3\text{H}_{10}$	
Formula weight	255.614 g/mol	
Wave length	0.71073 Å	
Crystal system, Space group	Monoclinic, $P2_1$	
Unit cell dimensions	$a = 5.052(1)$ $b = 9.194(2)$ $c = 10.388(2)$	$\alpha = \gamma = 90^\circ$ $\beta = 92.34^\circ$

**Powder X-ray Diffraction.** Using RICH SIEFERT X-ray Diffractometer with  $\text{CuK}\alpha$  ( $K\alpha = 1.5406$  Å) radiation, the grown crystal was subjected to powder X-ray diffraction studies at room temperature where Fig 3 shows the experimental Powder XRD pattern and Fig 4 shows the theoretically simulated XRD pattern of LHPCL single crystal. As a result both XRD patterns were found to be similar in comparison.



*Fig. 3. Experimentally obtained powder XRD pattern of LHPCL.*

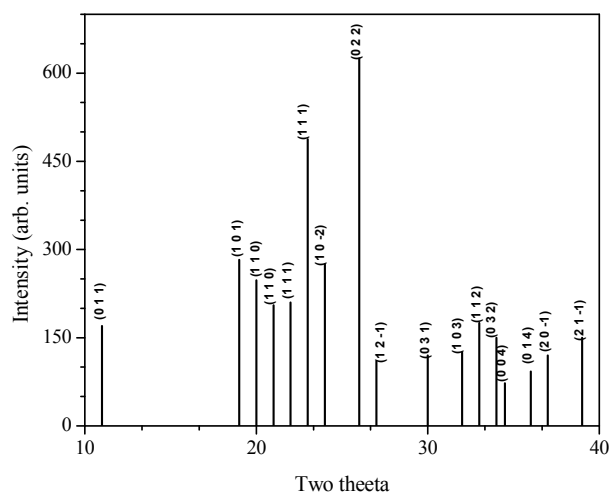


Fig. 4. Theoretically simulated powder XRD pattern of LHPCL.

**Computational Details.** By wavenumber calculations, the stability of the optimized geometries was confirmed and this gave the positive values for all the obtained wave numbers. A high degree of accuracy was made with vibrational frequency assignments by combining the theoretical results.

**Vibrational assignments.** The title molecule has got 72 ( $3N - 6$ ) normal vibrational modes and 26 atoms.  $\Gamma_{\text{vib}} = 49 A' \text{ (in-plane)} + 23 A'' \text{ (out-of-plane)}$  was the distribution of the 72 normal modes of LHPCL amongst the symmetry species. In Infrared absorption, all the 72 fundamental vibrations were found active. Table 2 shows the selected vibrational assignments of LHPCL for the experimental FT-IR frequencies along with the calculated frequencies.

Using KBr pellet technique on BRUKKER IFS FT-IR Spectrometer, the FT-IR spectrum of the grown crystal was recorded in the range  $400\text{cm}^{-1}$  to  $4000\text{cm}^{-1}$ . The title compound was carried out for the experimental IR spectrum which was compared with the calculation of B3LYP/6-31 G (d, p). Some bands in the calculated IR spectra were not observed in the experimental spectrum due to the fact that the computed wave numbers corresponds to gaseous phase of isolated molecular state and the observed wave numbers corresponds to the solid state spectra. Fig 5 shows the experimental FT-IR spectrum.

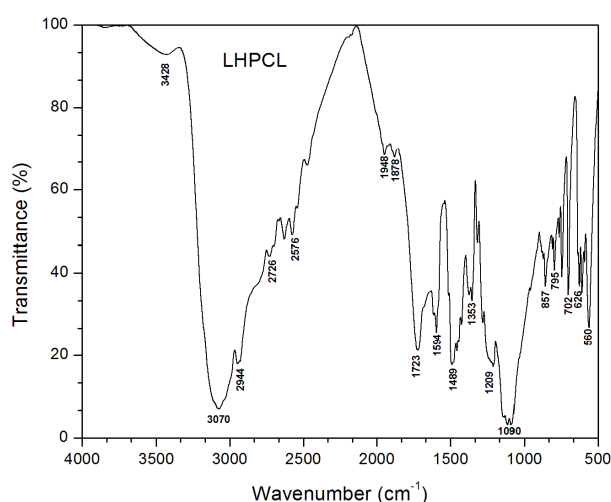


Fig. 5. Experimentally obtained FT-IR spectrum of LHPCL.

**C-Cl Vibrations.** For the title molecule the C–Cl stretching vibrations were found at bands  $623.83\text{cm}^{-1}$  and  $565.82\text{cm}^{-1}$  which was computed with the help of 6-31G (d, p) basis set. Due to C–Cl stretching vibrations, sharp peaks were occurred at  $560\text{cm}^{-1}$  and  $626\text{cm}^{-1}$  in the experimental spectrum. Hence the carbon atom acquired small positive charge whereas chlorine atom acquired a small negative charge. An increase in the absorption frequencies from the inductive effect of chlorine attracts electrons from the C–Cl bond which increased the force constant. The FT-IR simulated values were coincided by the experimental values of C- Cl vibrations.

**C-H Vibrations.** The nature and position of the substituent does not affect these vibrations. Due to C-H stretching vibrations, a sharp peak was occurred at  $3069.3475\text{cm}^{-1}$  using B3LYP/6-31 G (d, p) method and at  $3070\text{cm}^{-1}$  a sharp peak was shown for the experimental FT-IR. Due to the effect of C–H in-plane bending vibrations, the infrared peaks were identified at  $1489.048\text{cm}^{-1}$  (6-31G (d, p) basis set) and at  $1491\text{cm}^{-1}$  an experimental counterpart was seen. Using 6-31G (d, p) basis set, the vibration at  $1353.18\text{cm}^{-1}$  and peak at  $1353\text{cm}^{-1}$  was due to the C-H out of plane bending mode. The high organic nature was revealed from a prominent C-H vibration which was exhibited for the candidate material.

**HOMO-LUMO Gap.** The two energies that generally interact when we deal with interacting molecular orbitals were HOMO and LUMO of the compound. The interaction was made more strong which was allowed by these pair of orbitals. The orbitals of the compound were called as the frontier orbitals of the electrons as they lie at its outermost boundaries. The interaction was made more strong which was allowed by these pair of orbitals.  $-0.18352\text{a.u.}$  ( $4.9765\text{eV}$ ) was found to be the value of HOMO-LUMO energy gap for the compound LHPCL and Fig 6 shows the orbital picture. The energy gap reflects the chemical activity of the molecule which was revealed from the HOMO-LUMO energy gap of LHPCL. The ability to obtain an electron was represented by the LUMO which was an electron acceptor whereas the ability to donate an electron was represented by HOMO.

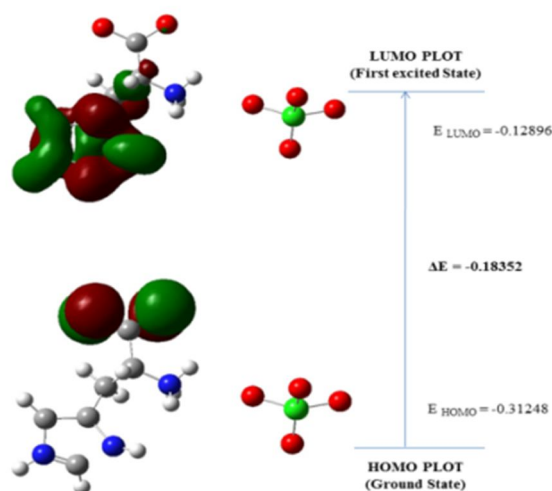


Fig. 6. HOMO – LUMO plot of LHPCL molecule.

**Nonlinear optical (NLO) test.** Kurtz and Perry powder technique was carried out for the compound LHPCL in order to confirm the nonlinear optical property [5]. By passing a Q-switched, mode locked Nd: YAG laser of  $1064\text{nm}$  and pulse width of  $8\text{ns}$  (spot radius of  $1\text{mm}$ ) on the powder sample of LHPCL, the SHG efficiency of the grown crystal was checked. Through an IR reflector, the input laser beam was passed and then it was directed on the microcrystalline powdered sample. The light emitted by the sample was detected by oscilloscope assembly and the photodiode detector. Taking KDP, which is a microcrystalline powder as the reference material, the SHG efficiency of the LHPCL crystal was evaluated.  $90\text{mV}$  and  $310\text{mV}$  were obtained as the SHG signal ( $532\text{nm}$ ) of KDP and LHPCL samples respectively for a laser input pulse of  $6.9\text{mJ}$ . The SHG efficiency of LHPCL was

3.44 times higher than that of KDP was observed.

**Summary.** By slow evaporation technique, at room temperature, the single crystals of LHPCL were grown. By XRD studies, the grown crystal was confirmed. Experimentally obtained FT-IR frequencies were compared by the theoretically calculated vibrational frequencies. For various vibrational frequencies, spectral assignments were carried out. For the selected moieties of LHPCL molecule, force constants and reduced masses were calculated. From HOMO-LUMO analysis, -0.18352 a.u (4.9765 eV) was found to be the value of molecular energy gap of LHPCL. The grown crystal had its SHG efficiency 3.44 times that of KDP, which was determined from the Kurtz SHG test.

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