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K Deepa, J Madhavan. Synthesis, Vibrational Spectroscopy, Thermal Analysis, Non-Linear Optical Properties and DFT Calculation of a Novel L-Phenylalanine Maleic Acid Single Crystals . Mechanics, Materials Science & Engineering MMSE Journal. Open Access, 2017, 10.2412/mmse.78.8.744 . hal-01503664

HAL Id: hal-01503664

<https://hal.science/hal-01503664>

Submitted on 7 Apr 2017

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Synthesis, Vibrational Spectroscopy, Thermal Analysis, Non-Linear Optical Properties and DFT Calculation of a Novel L-Phenylalanine Maleic Acid Single Crystals

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DOI 10.2412/mmse.78.8.744 provided by [Seo4U.link](#)

Keywords: crystal growth, DFT, HOMO-LUMO, FTIR, UV, TG/DTA, SHG.

ABSTRACT. Optically good quality new crystal of L-Phenylalanine maleic acid (LPM) was grown by slow evaporation technique. The crystalline nature of grown crystal is confirmed by X-ray diffraction analysis. Density functional theory (DFT) computations using (B3LYP) level with 6-31G (d,p) basis set gives optimized structure parameters of LPM molecule. Molecular energy gap of LPM was found by HOMO-LUMO analysis. Theoretically calculated vibrational frequencies are compared with experimentally obtained FT-IR frequencies. Optical absorption spectrum was recorded for the given crystal. Thermal stability and SHG studies were carried out for the grown crystal.

Introduction. Nonlinear optical (NLO) materials are active elements for optical communications, optical switching, optical mixing and electro-optic application [1]. Combination of amino acid with an organic compound has been proposed as a new candidate for NLO application, which crystallizes in non centrosymmetric space group. The proton donor carboxyl group (-COO) and the proton acceptor amino (-NH₂) group present in the amino acid contribute some physiochemical properties. The Density functional theory (DFT) calculation has now become the preferred method for understanding and predicting structure and reactivity in complex chemical system. DFT calculation along with vibrational spectral analysis is used as a promising tool to display a significant number of molecular properties of NLO materials [2]. Maleic acid forms crystalline maleate with various organic molecules through specific hydrogen bonding and π - π^* interactions. Which exhibit high value of second order polarizability [3]. L-Phenylalanine is an essential protein amino acid, which is used by the body to build neurotransmitter. A sequence of second order NLO active materials composed of L-phenylalanine have been synthesized, such as, L-phenylalanine benzoic acid [4], L-Phenylalanine nitric acid [5]. In the present work deals with the experimental and theoretical investigation of L-Phenylalanine maleic acid (LPM) single crystal.

Synthesis and crystal growth. High purity L-phenylalanine and maleic acid were taken in 1:1 molar ratio and dissolved in deionized water. The synthesized salt is purified by successive recrystallization process. After attaining the saturation, the equilibrium concentration of the solute was analyzed gravimetrically. After a period of 25 days, optically good quality single crystals of dimension upto 18 x 5 x 4 mm³ are harvested. The photograph of as grown single crystals of LPM crystal is shown in Fig. 1.

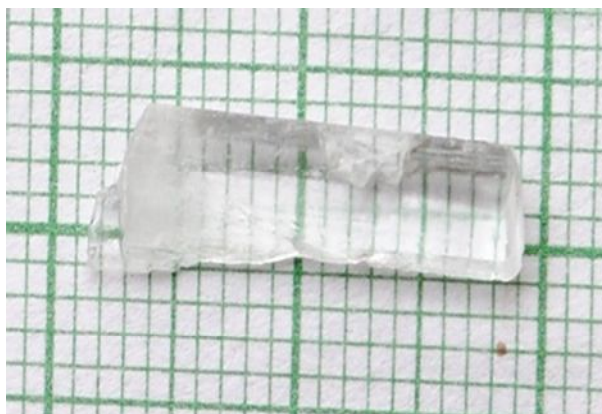


Fig. 1. Photograph of as grown LPM.

RESULTS AND DISCUSSION

Powder X-ray diffraction analysis. The LPM was subjected to powder X-ray diffraction analysis with a monochromatic Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$), recorded PXRD pattern of LPM is shown in Fig. 2. L-Phenylalanine maleic acid crystallizes in monoclinic structure with space group of P2 $_1$.

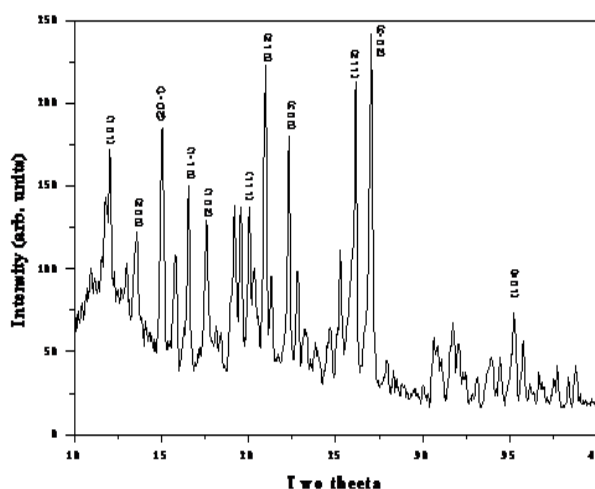


Fig. 2. Experimental Powder XRD pattern of LPM.

Computational Details. Quantum chemical Density functional theoretical (DFT) computations were performed using with the Gaussian program package using B3LYP functions combined with the 6-31 G(d, p) basis sets to derive the complete geometry optimizations and normal-mode analysis on isolated entities. Above said task was achieved using Gaussian03W program package, invoking gradient geometry optimization, implemented on Pentium core 2 duo/3 GHz processor with 2GB RAM personal computer [6].

Vibrational assignments. FT-IR spectrum of the grown crystal was recorded in the range 400 cm^{-1} to 4000 cm^{-1} , using KBr pellet technique on BRUKKER IFS FT-IR Spectrometer. The experimental FT-IR spectrum was reported in the Fig. 3. The theoretically simulated FT-IR spectrum at B3LYP/6-31+G (d, p) basis set was shown in Fig. 4. It is found that LPM molecule has 24 moiety and is in stable conformation with C $_1$ symmetry then exhibits 66 normal modes of vibrations. 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. 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} .

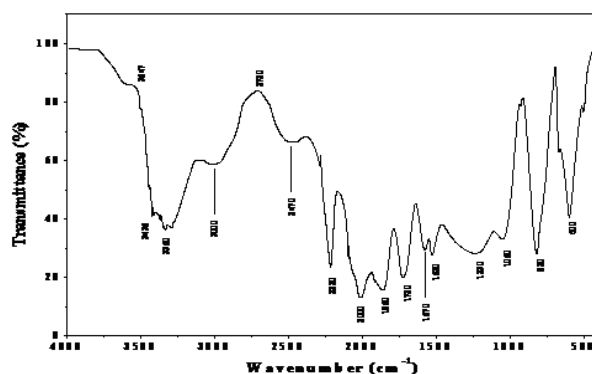


Fig. 3. Experimentally obtained FTIR spectrum of LPM.

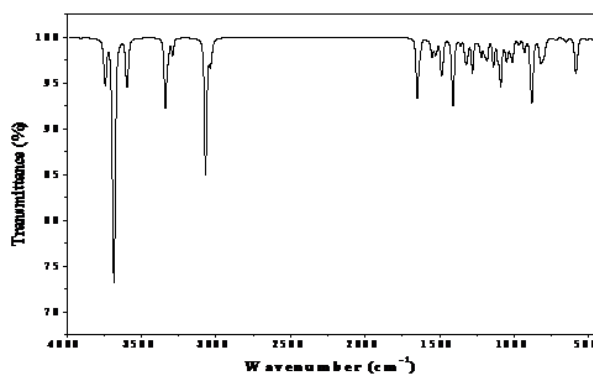


Fig. 4. Theoretically obtained FTIR spectrum of LPM.

Similarly, in our case a very strong FT-IR bands at 3905 , 3743 and 3684 cm^{-1} are assigned to O–H stretching vibrations. The hydrogen bonding effect through hydroxyl group leads to dimer conformation OH stretching mode calculated at 3595 cm^{-1} which is much closer to the FT-IR experimental observation at 3547 cm^{-1} . The O–H in-plane bending vibration in the phenols, in general lies in the region $1150\text{--}1250\text{ cm}^{-1}$. The O–H out-of-plane bending mode for the free molecule lies below 300 cm^{-1} and it is beyond the infrared spectral range of the present investigation. However, for the associated molecule the O–H out-of-plane bending mode lies in the region $517\text{--}710\text{ cm}^{-1}$ in both intermolecular and intra molecular associations, the frequency is at a higher value than in free O–H. The C–N ring stretching vibration bands occur in the region $1600\text{--}1500\text{ cm}^{-1}$. The present molecule exhibits this vibration in IR spectrum at 1650 cm^{-1} and the theoretically computed value at 1650 cm^{-1} by B3LYP method shows good agreement with recorded spectrum. C–N stretching absorption assigned in the region $1382\text{--}1266\text{ cm}^{-1}$. In the present work, the band observed at 1113 cm^{-1} in FT-IR spectrum has been assigned to C–N stretching vibration. The calculated frequency at 1012 cm^{-1} is in good agreement with experimental value. The C–O stretching vibration for this LPM molecule is obtained at 1380 and 1230 cm^{-1} in IR spectrum. Both the bands well coincided with theoretically calculated values at 1326 and 1223 cm^{-1} using B3LYP method. The band occurred at 216 cm^{-1} is assigned to C–O out plane bending occurred. The lowering of C–O stretching mode is attributed to the fact that the C–O group chelate with the other nucleophilic groups, thereby forming both intra and intermolecular hydrogen bonding in the crystal.

HOMO – LUMO Gap. In principle, there are several ways to calculate the excitation energies. The first, and the simplest one involves the difference between the highest occupied molecular orbital

(HOMO) and the lowest unoccupied molecular orbital (LUMO) of a neutral system. The indication of charge transfer from L-phenylalaninium to maleate moiety through the hydrogen bond, which is an important requirement to 0.05244 a.u. The calculated HOMO and LUMO energies clearly show that charge transfer occurs within the molecule. obtain large second order NLO response. The energies of the HOMO and LUMO, based on the optimized structure are computed as -0.10814 and -0.05570 a.u, respectively. The HOMO–LUMO energy gap is shown in Fig. 5.

SHG efficiency. The nonlinear optical conversion efficiency has been carried out using the Kurtz and Perry technique. When the Q-switched Nd: YAG laser was passed through LPM specimen, second harmonic signal of 532 nm is generated it was confirmed by the emission of green light. The second harmonic signal of 190 mW was obtained for LPM single crystal with reference to KDP (130 mW). Thus, the SHG efficiency of LPM single crystal is nearly 1.5 times greater than KDP.

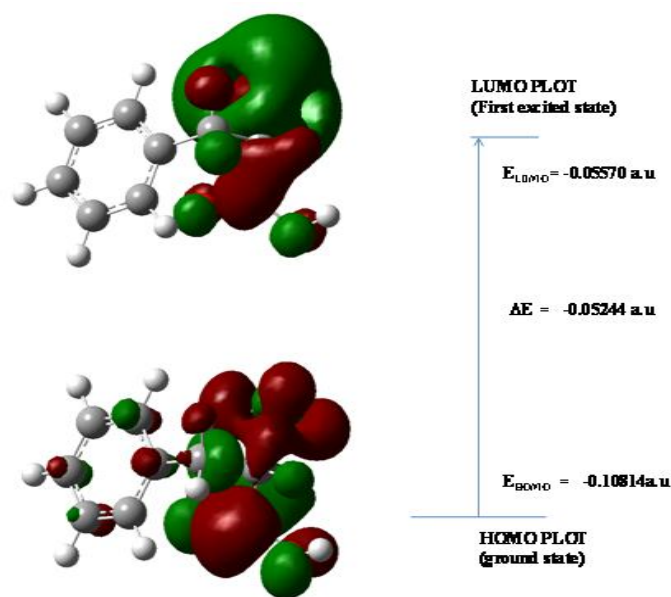


Fig. 5. HOMO –LUMO plot of LHDN at B3LYP/6-31 G (d, p).

UV-Vis-NIR spectrum. The optical absorption spectrum of LPM single crystal is shown in Fig. 6. The spectrum indicates that LPM crystal has minimum absorption in the region between 200–1200 nm. The lower cut off wavelength was around 275 nm. The values of the direct optical band gap E_g were obtained from the intercept of $(\alpha h\nu)^2$ versus $h\nu$ curve. The optical band gap is found to be 4.5 eV which is useful for gas sensing applications.

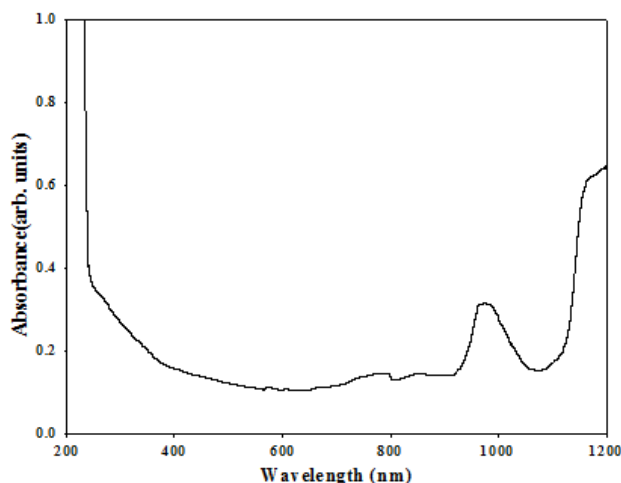


Fig.6. Optical absorption spectrum of LPM.

Thermal Analysis. The TGA/DTA analysis of LPM crystal was carried out in the temperature range of 200-1000°C in the nitrogen atmosphere and is shown in Fig. 7. From the TGA curve, it is clear that the material is stable up to 130°C before decomposition starts. In TGA, decomposition takes place after 151°C as the first stage. It goes up to 240°C which may be due to the loss of C_2H_4 and $2CO_2$, resulting in a loss of weight of 18.36%. Another weight loss of 36.71% at the second stage, noticed between the temperatures: 250–350 °C is due to the expulsion of C_6H_5 , CH_2 and NH_3 . The next stage of decomposition results in a loss of 27.54% between the temperature range 340–500 °C is due to the release of CO_2 . The next stage of decomposition results in a loss of 37.56% between the temperature range 500–800 °C is due to the release of CO. The remaining residue corresponds to carbon of the LPM crystal. The sharp DTA peaks at 180 and 300 °C are attributed to the decomposition of the material, which match well with the first and second stage of decomposition in the TGA curve, respectively.

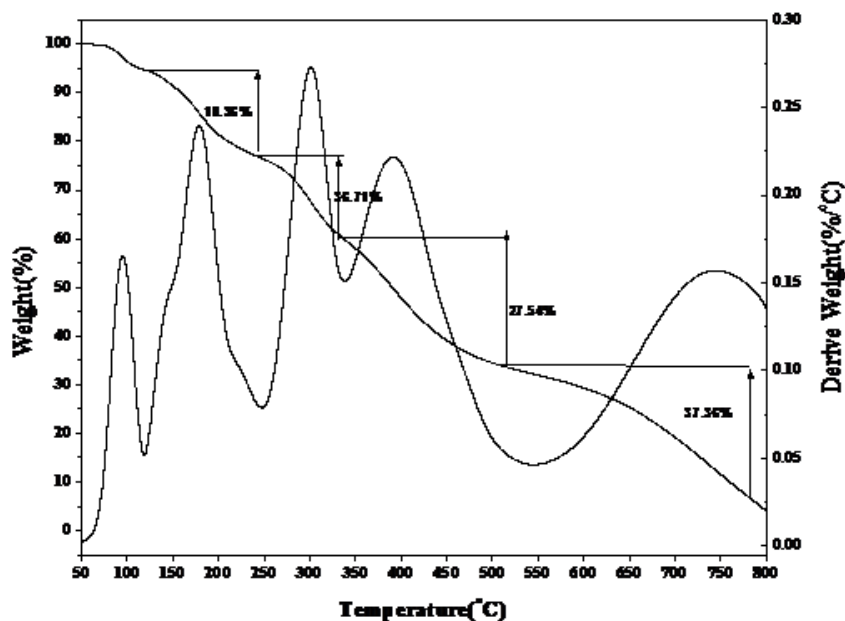


Fig. 7. TG-DTA curves of LPM single crystals.

Summary. L-Phenylalanine maleic acid single crystals were grown by slow evaporation technique at room temperature. Powder XRD confirmed the grown crystal. Theoretical and experimental

Spectroscopic studies exemplify the presence of various functional groups in the molecule. A frontier molecular orbital analysis gives the HOMO-LUMO energy gap value. The lower UV cut-off wavelength of the sample observed at 275 nm. The NLO efficiency was estimated. The promising crystal growth characteristics and properties of LPM crystal indicate it as a potential material for photonic, electro-optic and SHG device application.

References

- [1] S. Natarajan, G. Shanmugam, S.A. Martin Britto Dhas, “Growth and characterization of a new semi organic NLO material L-tyrosine hydrochloride,” *Cryst. Res. Technol*, Vol. 43, pp. 561-564, 2008, DOI.10.1002/crat.200711048.
- [2] C. Ravikumar, I. Hubert Joe, D. Sajan, “Vibrational contributions to the second-order nonlinear optical properties of π -conjugated structure acetoacetanilide,” *Chem. Phys*, Vol. 369, pp. 1-7, 2010, DOI. 10.1016/j.chemphys.2010.01.022.
- [3] P. VinothKumar, R. Mohankumar, R. Jeyavel, A. Bhasharan, “Synthesis. Growth, structural, optical, thermal and mechanical properties of an organic Urea maleic acid single crystals for nonlinear optical applications,” *Opt. Laser. Tech*, Vol. 81, pp. 145-152, 2016, DOI. 10.1016/j.optlastec.2016.02.004
- [4] S. Tamilselvan, M. Vimalan, I. Vetha Potheher, S. Rajasekar, R. Jeyasekaran, M. Antony Arockiaraj, J. Madhavan, “Growth, thermal, dielectric and mechanical properties of L-phenylalanine–benzoic acid, A nonlinear optical single crystal,” *Spectrochimica Acta Part A*, Vol. 114, pp. 19-26, 2013, DOI. 10.1016/j.saa.2013.05.017
- [5] M. Lydia Caroline, S. Vasudevan, “Growth and characterization of L-phenylalanine nitric acid, a new organic nonlinear optical material,” *Mater. Lett*, Vol. 63, pp. 41-44, 2009, DOI. 10.1016/j.matlet.2008.08.059.
- [6] J.B. Foresman, in: E. Frish (Ed), “Exploring chemistry with Electronic structure Methods: a Guide to using Gaussian, Gaussian Inc.,” Pittsburg, PA, 1996.

Cite the paper

K. Deepa, J. Madhavan, (2017). [Synthesis, Vibrational Spectroscopy, Thermal Analysis, Non-Linear Optical Properties and DFT Calculation of a Novel L-Phenylalanine Maleic Acid Single Crystals](#). *Mechanics, Materials Science & Engineering*, Vol 9. Doi [10.2412/mmse.78.8.744](#)