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Linear and nonlinear optical properties of L-phenylalaninium maleate a promising nonlinear optical single crystal

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ABSTRACTS

Single crystals of L-phenylalaninium maleate (LPM) were grown by slow solvent evaporation technique at room temperature. Good optical grade single crystals of size 10×4×3mm^3 are obtained. The structure of the grown crystal was obtained from single crystal XRD. It is observed from the XRD data that LPM crystal belongs to monoclinic system with space group $P2_1$. The Fourier transform infrared analysis (FT-IR) was carried out and the various functional groups in the sample were identified. The optical absorption spectrum of the sample was recorded in the range 200-2000 nm. The UV-Vis-NIR spectrum shows low absorption in the entire visible region. The second harmonic generation efficiency of the powdered sample was measured using Nd:YAG Q-switched laser with first harmonic output of 1064 nm and KDP was taken as the reference material. The variation of dark current and photo current with the applied field was studied using a Keithly 480 picoammeter. Photoconductivity study confirms the negative photoconductive nature of LPM.

INTRODUCTION

The importance of amino acids in NLO applications is due to the fact that all the amino acids have chiral symmetry and crystallize in noncentrosymmetric space groups [1]. Many numbers of natural aminoacids are individually exhibiting the nonlinear optical properties because they are characterized by chiral carbons, a proton-donating carboxyl group and the proton-accepting amino group. The crystal structures of amino acids and their complexes have provided a wealth of interesting information to the patterns of their aggregation and the effect of other molecules and ions on their interactions and molecular properties [2]. In solid state an amino acid contains a protonated amino group (NH_3^+) and deprotonated carboxylic acid group (COO^-), which provide the ground state charge symmetry of the molecule. The dipolar nature exhibits peculiar physical and chemical properties in amino acids which make them ideal candidates for NLO

applications [3]. Maleic acid with relatively large π conjugation is yet another amino acid NLO material. Efforts have been taken to combine amino acids with interesting organic acid, (Maleic acid) to produce outstanding materials to challenge the existing prospective materials. These materials exhibit promising structural background in view of their zwitterionic and protonated forms and structural stabilization with hydrogen bonding. Maleate complexes of α-amino acids are reported for its potential second harmonic generation [4, 5]. The earlier works on LPM were restricted to the solving of crystal structure and other properties are not yet reported.

Synthesis

High purity L-phenylalanine (Merck 99%) and maleic acid (Analar grade) were taken in 1:1 molar ratio and dissolved in deionized water. The reaction is as follows,

$C_6H_5CH_2CH\ (NH_2)^+\ C_4H_4O_4 \longrightarrow C_6H_5CH_2CH\ (NH_3)^+\ COOH\ C_4H_3O_4^-$

Purification is an important step in order to obtain single crystals of high quality. Hence the synthesized salt is purified by successive recrystallization process.

2.1 Solubility of LPM

Solubility corresponds to saturation i.e. to equilibrium between a solid and its solution at a given temperature and pressure. Thermodynamically, this means that the chemical potential of the pure solid is equal to the chemical potential of the same solute in the saturated solution. The growth rate of a crystal depends on its solubility and temperature. Solubility data of a material govern the amount of material, which is available for the growth and hence, defines the total size limit. Solvent and solubility factors define supersaturation, which is the driving force for the rate of crystal growth. Hence, for a material to grow as a crystal, determination of its solubility in a particular solvent is an essential criterion.

The synthesized salt of LPM was further purified by repeated crystallization process. A 250 ml glass beaker containing 100 ml of deionized water was placed in the temperature bath. The initial temperature of the bath was set at 30 ^oC. The beaker was closed with an acrylic sheet containing a hole at the center through which a spindle from an electric motor, placed on the top of the sheet was introduced into the solution. A teflon paddle was attached at the end of the rod for stirring the solution. The synthesized salt was added in small amounts and stirring of the solution by a motorized stirrer was continued till the formation of precipitate, which confirmed the saturation of the solution. The stirring was further confirmed to have uniform temperature and concentration throughout the entire volume of the solution. After attaining saturation, the equilibrium concentration of the solution was analyzed gravimetrically. A 20 ml of the clear supernatant liquid was withdrawn by means of a warmed pipette and the same was poured into a clean, dry and weighed empty petri dish. The solution was then kept for slow evaporation in a heating mantle till the solvent was completely evaporated. The mass of LPM in 20 ml of solution was determined by weighing the petri dish with salt and hence the amount of LPM salt (in gram) dissolved in 100 ml of water was determined. The same procedure was repeated for various temperatures 30, 35, 40, 45 and 50 °C and the solubility of LPM was estimated. Figure 1 shows the solubility curve of LPM.

2.2 Growth of LPM single crystals

The saturated solution is prepared for the growth of LPM single crystals according to solubility

data. Within a week seed crystals are formed by spontaneous nucleation. After a period of 25 days, optically good quality single crystals of dimension up to 10 x 4 x 3 mm^3 are harvested. It is evident that the grown crystals exhibits needle shaped morphology. The photograph of as grown single crystals of LPM crystal is shown in Figure 2.

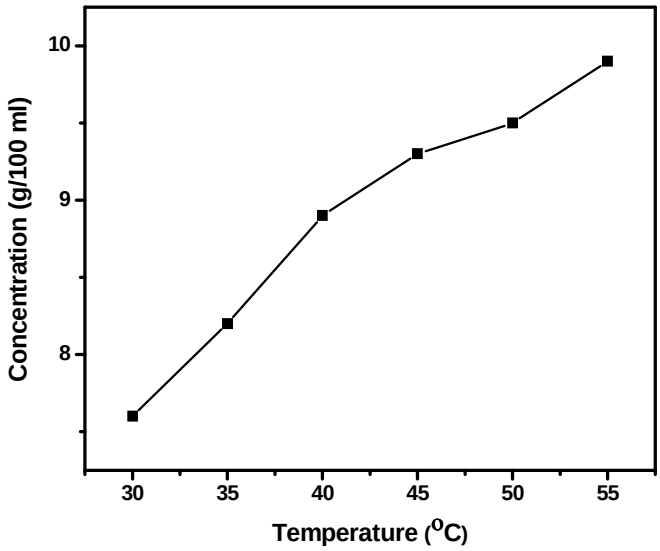

Figure 1 Solubility curve of LPM

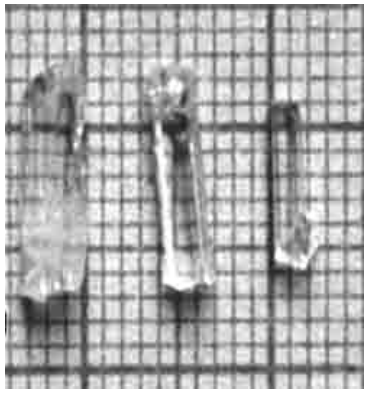

Figure 2 Photograph of as grown single crystal of LPM

RESULTS AND DISCUSSION

3.1 Single crystal XRD analysis

The single crystal XRD analysis data of LPM indicates that it crystallizes in the monoclinic system with $P2_1$ space group and cell parameters are presented in Table 1. The single crystal XRD data determined in the present work is in good agreement with the reported data [6].

Table 1: Single crystal XRD data of LPM

Empirical formula	$C_{13}H_{15}NO_6$
Crystal system	Monoclinic
Space group	$P2_1$
a (Å)	11.101
b (Å)	5.410
c (Å)	11.510
α	90°
β	101.1°
γ	90°
Volume (Å)^3	676

3.2 FT-IR analysis

Figure 3 shows FT-IR spectrum of LPM. In the FT-IR spectrum, the peak at 3423 cm^{-1} is assigned to OH stretch of water. It is supported by its bending mode at 1625 cm^{-1}. The OH stretch of maleate should also occur close to 3423 cm^{-1}. But it is not clearly resolved. The peak at 3177 is due to N-H vibration of NH_3^+. The aromatic C-H vibration gives its peak at 3032 cm^{-1}. The aliphatic C-H vibration occurs at 2971 and 2948 cm^{-1}. Hydrogen bonding of maleate OH water and NH of NH_3^+ shows peaks at 2714 and 2606 cm^{-1}. The C = O vibration of maleate occurs at 1723 cm^{-1}. The asymmetric and symmetric bendings of NH_3^+ occur at 1610 and 1498 cm^{-1}. The asymmetric and symmetric vibrations of CO_2 occur at 1573 and 1386 cm^{-1}. The bending mode of CH_2 gives peaks at 1358 and 1458 cm^{-1}. The C-COO vibration gives peaks at 1270 and 1230 cm^{-1}. The C-H bending mode of maleate gives a shoulder in the lower energy region of the peak at 700 cm^{-1}. The aromatic C-H bend modes are due to peaks at 700 and 739 cm^{-1}. The peaks at 576 and 520 cm^{-1} are due to torsional oscillation of NH_3^+. Hence from the IR spectral analysis presence maleate in association with phenylalanine is clearly evident. The FT-IR frequency assignment of LPM is presented in Table 2.

3.3 Optical absorption studies

The UV-Vis-NIR response curve of LPM (Figure 4) shows very low absorption in the visible and NIR region. LPM has a low cut-off wavelength when compared with the other members of the amino acid family. The UV cut-off wavelength of LPM is around 240 nm which is lower than some of the amino acid single crystals such as L-arginine tetrafluoroborate (LAFB) (270 nm) and L-arginine maleate (LARM) (300 nm) [4, 7]. The optical energy gap of LPM single crystal has been calculated using Tauc's plot (Figure 5). The band gap energy is found to be 5 eV.

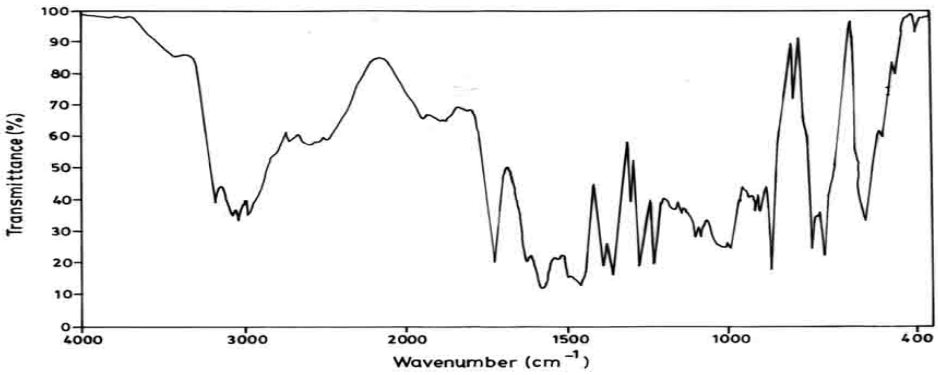

Figure 3 FT-IR spectrum of LPM

Table 2: FT-IR frequency assignments for LPM

Wavenumbers (cm^{-1})	Assignments
3423	O-H stretching
3177	NH vibration of NH_3^+
3032	aromatic C-H vibration
2971, 2948	aliphatic C-H vibration
1723	C=O vibration
1610	NH_3^+ asymmetric bending
1498	NH_3^+ symmetric bending
1573	asymmetric CO_2 vibration
1358, 1458	CH_2 bending
1270, 1230	-COO- vibration
700	C–H bending vibration
576, 520	Torsional oscillation of NH_3^+

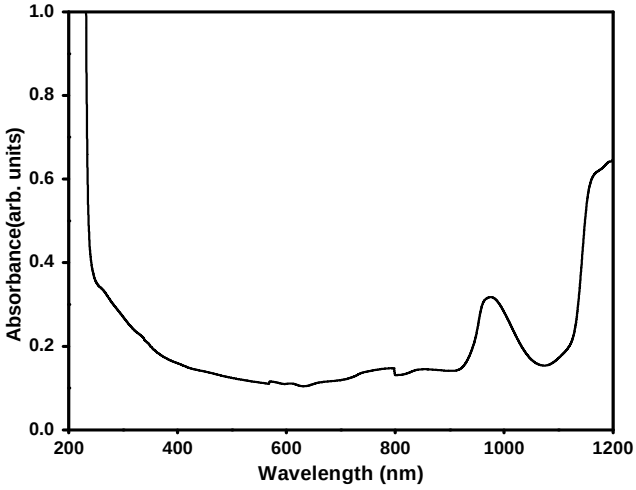

Figure 4 Optical absorption spectrum of LAO

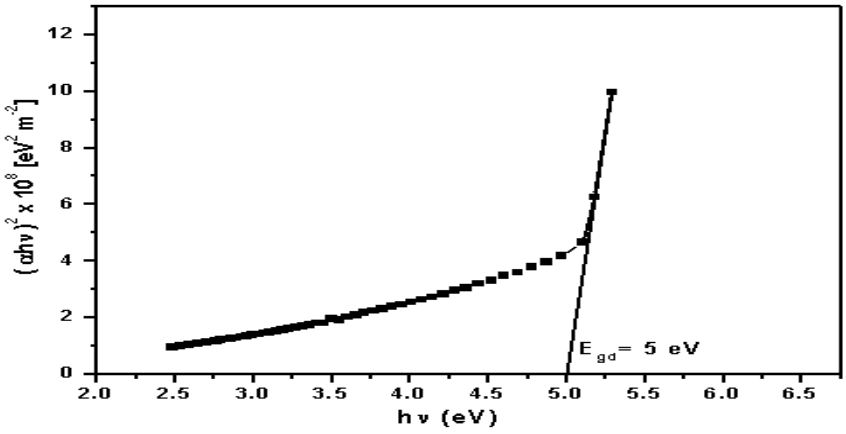

Figure 5 Tauc's plot of LAO

3.4 NLO studies

The powdered sample of LPM was illuminated using the fundamental beam of 1064 nm from Q-switched Nd: YAG laser pulse energy 6 mJ/pulse, pulse width of 10 ns at a repetition rate of 10 Hz. Second harmonic signals (532 nm) of 55 and 84 mV are obtained through KDP and LPM samples respectively. Thus the SHG efficiency of LPM is 1.5 times that of KDP. Emission of green radiation from the sample confirms the presence of NLO property. It is seen that the SHG efficiency of LPM is greater when compared with some of the amino acid analogs such as LAA (0.30), LAFB (0.8) and LARPCL (1.2) [7].

3.5 Photoconductivity study

Photoconductivity measurements were made using Keithley 485 picoammeter. The dark current was recorded by keeping the sample unexposed to any radiation. Figure 6 shows the variation of both dark current (I_d) and photocurrent (I_p) with applied field. It is seen from the plots that both I_d and I_p of the sample increase linearly with applied field. It is observed from the plot that the dark current is always higher than the photo current, thus confirming the negative photoconductivity.

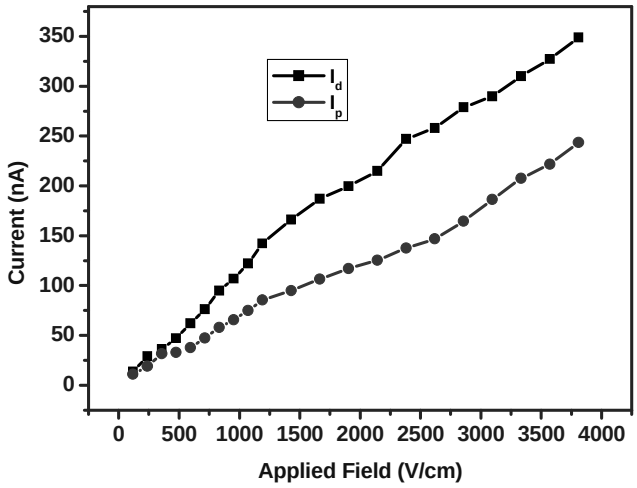

Figure 6 Field dependent photoconductivity of LPM single crystal

CONCLUSION

Optically good quality single crystals of LPM were grown by slow solvent evaporation technique. Single crystal XRD confirms the identity of the grown crystal. The optical absorption spectrum confirms that the crystal has very low absorption in the entire visible and infrared region, with lower UV cut-off wavelength around 240 nm, which is an essential consideration for NLO crystals. The Photoconductivity study confirms the negative photoconductivity nature of the grown crystal.

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