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Growth and physicochemical properties of L-phenylalaninium maleate: A novel nonlinear optical crystal

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Introduction

ABSTRACT

Single crystals of novel organic nonlinear optical material, L-phenylalaninium maleate (LPM) having dimensions up to $10 \times 6 \times 6$ mm³ were grown by slow evaporation solution growth technique at room temperature. The grown crystals were confirmed by single crystal X-ray diffraction studies and the various functional groups were identified by FT-IR spectroscopic analysis. The optical properties were studied by optical absorption, second harmonic generation (SHG), photoconductivity and photoluminescence (PL) studies and reported for the first time. The optical band gap energy and SHG efficiency were found to be 4.85 eV and 1.5 times higher than KDP crystals. Negative photoconducting nature was confirmed by photoconductivity studies. Photoluminescence studies confirm the suitability of the sample for blue and green radiations. The title compound was also subjected to TG/DTA analysis and dielectric studies. Layer like growth pattern was analyzed by SEM micrograph.

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Organic nonlinear optical (NLO) materials are attracting a great deal of attention due to their potentially high nonlinearity and rapid response in the electro-optic effect compared to inorganics. New molecular organic compounds with one or more aromatic systems in conjugated positions, leading to highly efficient charge transfer systems have been actively studied. Most of the organic crystals are composed of aromatic molecules that are substituted with π electron donors and acceptors which exhibit intermolecular charge transfer resulting in high SHG efficiency. These compounds must crystallize in a non-centrosymmetric class in view of applications making use of quadratic optically nonlinear effects. Organic compounds are formed by weak Van der Waal's and hydrogen bonds and possess high degree of delocalization [1]. Hence they are optically more nonlinear than inorganic materials. Some of the advantages of organic materials include flexibility in the methods of synthesis, scope for altering the properties by functional substitution, inherently high nonlinearity, high damage resistance, etc. [2]. Organic materials with delocalized π electrons usually display a large NLO response which makes it most resourceful for various applications including optical communication, optical computing, optical information processing, optical disk data storage, laser fusion reactions and laser remote sensing [3]. In solid state amino acid contains a protonated amino group (NH₃⁺) and deprotonated carboxylic acid group (COO⁻). The dipolar nature exhibits peculiar physical and chemical properties in amino acids which make them ideal candidates for NLO applications [4–6]. 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 their potential second harmonic generation [7-10]. Earlier, synthesis, SHG and thermal properties of LPM were reported by Anbuchezhiyan et al. [11]. In the present investigation, the size of the crystal was improved compared to the reported size [11]. The grown crystals were characterized by single crystal X-ray diffractometry (XRD), FT-IR, UV-Vis-NIR, thermal and SHG analyses. Also the grown crystals were subjected to dielectric, photoconductivity, photoluminescence studies and SEM analysis and reported for the first time.

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Experimental procedure

Synthesis and crystal growth

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

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

Based on the solubility data, the supersaturated solution was prepared and the solution was stirred for 3–4 h. Then the solution was covered by Teflon sheet and kept for nucleation. A number of small holes were made on the top of the Teflon sheet for evaporation of the solution. Due to spontaneous nucleation, optically quality transparent single crystals were grown in a period of 25–30 days with dimensions up to $16 \times 2 \times 2 \text{ mm}^3$ by slow solvent evaporation technique. The size of the crystal was improved by successful recrystallization. The dimension of the grown crystal was improved compared to the reported dimensions [11]. The photograph of as grown single crystal of LPM crystal is shown in Fig. 1. From the photograph, it is evident that the grown crystals exhibit needle shaped morphology.

Characterization

In order to confirm the grown crystal, single crystal X-ray diffraction studies were carried out using ENRAF NONIUS CAD4-F single X-ray diffractometer. The various functional groups present in LASP crystal were identified and conformed by the FT-IR study. The spectrum was recorded in the range $4000-400 \text{ cm}^{-1}$ using BRUKER IFS-66V spectrometer by KBr pellet technique. The UV-Vis-NIR analysis of LASP crystal was carried out between 200 and 2000 nm covering the entire near ultra violet, visible and infrared regions using the VARIAN CARY 5E model spectrophotometer. The thermal behavior of the grown crystal was characterized using SDT Q600 thermal analyzer in nitrogen atmosphere at a heating rate of 20 °C/min in the temperature range of 20-1000 °C. The measurement of dielectric constant and dielectric loss as a function of frequency and temperature were calculated using HIOKI 3532-50 LCR HITESTER in the frequency range 100 Hz-5 MHz. The SHG efficiency was measured by employing Kurtz powder technique [12]. The photoluminescence of the sample was recorded by VARIAN spectrometer with 2.5 kV fluorescence lamp. The measurements of photocurrent (I_p) and dark current (I_d) were carried out by a pico Ammeter (Keithley 485). A well polished sample was attached to the microscopic slide on which two copper electrodes were fixed with silver paint at known distance of 1 mm. The applied field was varied from 150 to 2650 V/cm. For measuring the dark current,



Fig. 1. Photograph of grown single crystal of LPM.

the sample was kept unexposed from any radiation. After measuring the dark current, the photocurrent was measured by illuminating the sample with a halogen lamp of 100 W power. A spot of light on the sample was focused with the help of a convex lens. The resulting photocurrent was measured by varying the applied field for the same range. Surface morphology of the grown crystal was analyzed by Scanning Electron Microscopy (SEM) using JEOL/EO-JSM-5610 Scanning Electron Microscope.

Results and discussion

Single crystal XRD

The single crystal XRD analysis data of LPM indicate that it crystallizes in the monoclinic system with $P2_1$ space group and the cell parameters are a = 11.0564 Å, b = 5.3321 Å and c = 11.4710 Å. The single crystal XRD data of LPM are presented in Table 1. The single crystal XRD data determined in the present work are in good agreement with the reported data [13].

FT-IR analysis

Fig. 2 shows FT-IR spectrum of LPM. From the spectrum, it is observed that 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 cm^{-1} is due to N–H vibration of NH₃⁺. 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 NH₃⁺ give peaks at 2714 and 2606 cm⁻¹. The C=O vibration of maleate occurs at 1723 cm⁻¹. The asymmetric and symmetric vibrations of NH₃⁺ occur at 1610 and 1498 cm⁻¹. The asymmetric and symmetric vibrations of CO₂ occur at 1573 and 1386 cm⁻¹. The bending modes of CH₂ give peaks at 1358 and 1458 cm⁻¹. The C-COO vibration give 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 torsional oscillation of NH_3^+ gives a peak at 576 and 520 cm⁻¹. Hence from the IR spectral analysis the presence of maleate in association with phenylalanine is clearly evident.

Optical absorption studies

The UV–Vis–NIR response curve of LPM (Fig. 3) shows very low absorption in the visible and NIR regions. 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) [14,7]. The optical energy gap of LPM single crystal has been calculated

Table 1	
Single crystal XRD data of LPM crystal.	

L-Phenylalaninium maleate	Crystal data
Empirical formula	$C_{13}H_{15}NO_{6}$
Crystal system	Monoclinic
Space group	$P2_1$
a (Å)	11.057
b (Å)	5.330
<i>c</i> (Å)	11.472
α (°)	90
β (°)	101
γ (°)	90
Volume (Å ³)	676
Ζ	2





Fig. 3. UV-Vis-NIR spectrum of LPM crystal.

using Tauc's plot [15]. A plot is drawn between hv and $(\alpha hv)^2$ (Fig. 4). By extrapolating the straight line portion of the curve, the optical band gap energy was determined and it was found to be 4.85 eV.

NLO studies

The powdered sample of LPM was illuminated using the fundamental beam of 1064 nm from Q-switched Nd:YAG laser with pulse energy 6 mJ/pulse and pulse width of 10 ns at a repetition rate of 10 Hz. Emission of green radiation from the sample confirms the presence of NLO property. Second harmonic signals (532 nm) of 55 and 85 mV were obtained through KDP and LPM samples, respectively. Thus the SHG efficiency of LPM is 1.5 times higher than that of KDP. It is seen that the SHG efficiency of LPM is greater when compared with some of the amino acid analogs such as LAFB (0.8) [13] and LARPCL (1.2) [16].

Thermal analysis

Thermograms shown in Fig. 5 are illustrating the simultaneous record of TGA and DTA of LPM. As indicated by the TGA curve the initial decomposition of the sample starts at about 140.90 °C. Since it is beyond 100 °C, there is no water of crystallization present in



Fig. 4. Tauc's plot of LPM.

LPM. During the next stages, maleic acid in the crystal decomposes and becomes anhydride [9] and results in further release of CO_2 and CO molecules at 197.52 and 278.75 °C at the third stage. The reactions of simplest amino acids induced by heating include the condensation reactions of carboxyl and amino groups leading to the formation of peptide bonds. More volatile substances such as CO and CH₄ are liberated around 396.91 °C. Further heating results in the liberation of NH₃ molecule at 523.69 °C.

The endothermic peak observed at 127 °C in DTA trace corresponds to the melting point of the sample. This is attributed to utilization of the thermal energy to overcome the valence bonding between the L-phenylalaninium cation and maleate anion, which happens in the initial stage of decomposition. This endotherm and other endotherms that follow at high temperatures coincide with different stages of weight loss in TGA.

Dielectric studies

Studies on the frequency and temperature dependence of dielectric properties unveil useful information about structural



Fig. 5. TG/DTA thermogram of LPM.

changes, defect behavior and transport phenomena. Figs. 6 and 7 show the variation of dielectric constant and dielectric loss with log frequency at different temperatures. The dielectric constant of the materials is due to the contribution of electronic, ionic, orientational and space charge polarizations, which depend on the frequencies. The influence of space charge polarization is noticeable in the low frequency region. Materials used for device fabrication in photonics industry demand the low value of dielectric constant [17].

From Fig. 7 it is observed that the dielectric loss is strongly dependent on the frequency of the applied field as in the case of dielectric constant. In the low frequency region, dielectric loss is more due to the loss associated with ionic mobility [17]. However, the low value of dielectric loss at high frequency implies that this

parameter is of vital importance for NLO materials in their application [18].

Photoluminescence studies

PL spectrum of the sample was recorded between 300 and 800 nm. A graph was plotted against PL intensity and wavelength. Fig. 8 shows the variation of PL intensity with wavelength. From the figure the intense emission peak was appeared close to 400 and 550 nm, which may be due to the emission of blue radiation. This is because of aromatic ring and their contribution to molecular association through Van der Waal's force in the crystal. The broadening of emission illustrates much interaction of carboxyl group with the lattice. The sharp emission peaks observed between 500



Fig. 6. Variation of dielectric constant with log frequency for LPM.



Fig. 7. Variation of dielectric loss with log frequency for LPM.



Fig. 8. Photoluminescence spectrum of LPM crystal.



Fig. 9. Field dependent photoconductivity of LPM.



Fig. 10. SEM micrograph of LPM single crystal.

and 550 nm are attributed due to the influence of maleate group and which may be due to the emission of green radiation. Hence the photoluminescence studies confirm the suitability of the material in blue and green regions.

Photoconductivity studies

Fig. 9 shows the variation of field dependent dark current and photo current of LPM crystal. It is observed that both the dark and photo currents increase linearly with the applied electric field, but the photocurrent is less compared to the dark current which is termed as negative photoconductivity. The negative photoconductivity exhibited by the sample may be due to the reduction of the number of charge carriers in the presence of radiation [19].

SEM analysis

The SEM micrographs of LPM were taken at room temperature with magnification factor 75 in the operating voltage of 20 kV and are shown in Fig. 10. The figure indicates the layer like growth pattern. Also few micro particles are seen on the surface of the crystal.

Conclusion

Optically good quality single crystals of LPM were grown by slow solvent evaporation technique. Single crystal XRD confirms that the grown crystal belongs to monoclinic crystal system with P2₁ space group. The optical absorption spectrum confirms that the crystal has very low absorption in the entire visible and infrared regions, with lower UV cut-off wavelength around 240 nm, which is an essential consideration for NLO crystals. Thermogravimetric analysis implies that the grown crystal was thermally stable up to 127 °C. The photoconductivity study confirms the negative photoconductivity nature of the grown crystal. The dielectric studies indicate that the dielectric constant and dielectric loss decreases with increasing frequency. The SEM results revealed the surface morphology of the as grown crystal. The suitability of the material in the blue and green emission regions was confirmed by photoluminescence studies.

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