Growth and Characterization of Pure and Doped L- Phenylalanine Maleate Single Crystals

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Abstract—In the present investigation, influence of rare earth metal (La^{3+} and Nd^{3+}) dopant on the structural, linear and nonlinear optical properties of L- Phenylalanine maleate (LPM) crystals has been studied successfully. The exact weight percentage of the La^{3+}and Nd^{3+} present in doped crystals were determined by Inductively Coupled Plasma analysis. Powder X-ray diffraction studies were carried out for the pure and doped crystals. Nonlinear optical properties were also studied by SHG studies.

*Keywords—Powder XRD, NLO, ICP, FT-IR, UV-Vis*

I.   INTRODUCTION

During the last three decades, much progress has been made in the development of new and better nonlinear optical (NLO) materials having large nonlinear optical coefficients. Nonlinear optical (NLO) materials are of much importance because of its extended applications, especially to develop new laser sources [1]. In recent years, researchers have identified amino acid based nonlinear optical crystals with better linear and nonlinear optical properties. The wider choice of materials, improved high non-linearity, low transformation temperature, fast response and high transparency make these systems more demanding than any other systems. Nonlinear optical phenomena have got a tremendous interest after the advent of laser sources, and they play a vital role in the development of laser technology [2]. Development of high efficiency NLO crystals is of great importance to extend the frequency range provided by normal Laser source into Ultraviolet and Infrared regions [3]. The organic NLO crystals have attracted because of the low cost and flexibility as they posses some special properties of large optical non-linearity and low cut-off wavelength [4]. L-Phenylalanine is one of the essential amino acid and must be provided in the diet for vertebrates. Phenylalanine is 'non-functional' indicating that it does not participate directly in catalytic and enzymatic action. It plays an important role in determining the secondary structure and forming specificity for catalytic action [5]. Our present study is growth and characterization of pure and doped L-Phenylalanine Maleate (LPM) single crystal which is an excellent organic crystal. LPM single crystals (pure and doped) were grown by slow evaporation technique at room temperature. Good quality, transparent and defect free tiny crystals formed due to spontaneous nucleation were used as seeds to grow bulk crystals. The grown crystals were characterized by Powder XRD, UV-Vis and FT-IR analysis

II.   EXPERIMENTAL PROCEDURE

Aqueous solution of pure, La^{3+}and Nd^{3+} doped LPM were prepared by dissolving stoichometric L-phenylalanine (Merck 99%) and maleic acid (Analar grade) in double deionized water. The solubility of the pure and doped LPM crystals were measured at different temperatures and the solubility curves were drawn in Fig. 1. From the solubility curve, it is observed that the solubility increases with temperature both for pure and doped. Seed crystals were formed due to spontaneous nucleation and among them tiny crystals with perfect shapes were used for growth experiments.

The pure and doped LPM crystals were grown by slow evaporation technique at room temperature (30°C). The reaction that takes place between L-phenylalanine and maleic acid in water medium is as follows:

$$C_6H_5CH_2CH\,(NH_2) + C_4H_4O_4 \longrightarrow C_6H_5CH_2CH\,(NH_3)\,^+COOH\ C_4H_3O_4{}^-$$
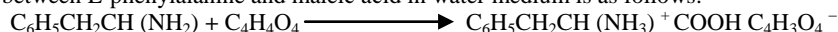
The same procedure is applied to grow the metal (La^{3+}and Nd^{3+}) doped crystals by adding 2 mol % of La^{3+}and Nd^{3+} to the LPM solution respectively. The crystals are found to be transparent and free from defects. Fig. 2 shows the photographs of the as grown pure and doped crystals nearly in a period of 40 days.
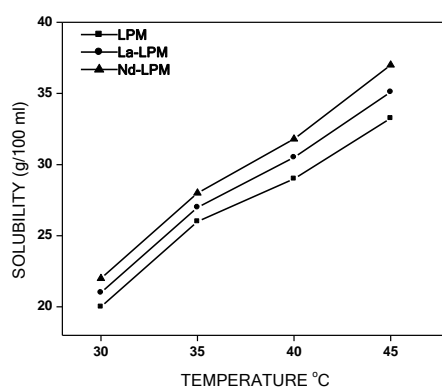
Fig. 1 Solubility curves of pure and doped LPM crystals

III.   CHARACTERIZATION

A.   Powder XRD studies

The structural properties of single crystals of pure and doped LPM have been studied by X-ray powder diffraction technique. Powder X-ray diffraction studies of pure, La^{3+} and Nd^{3+} doped LPM crystals were carried out, using Siemens D500 X-ray diffractometer with Cu K_α ($\lambda = 1.5418$Å) radiation. The samples were scanned for 2θ values from $10°$ to $40°$ at a rate of $2°$ /min. Figure 3 shows the Powder XRD pattern of the pure and doped LPM crystal.

The diffraction patterns of the pure and doped LPM crystals have been indexed by least square fit method. The lattice parameter value of the pure LPM crystal has been calculated and is well matched with the reported literature [6]. It is seen that both the pure and doped crystals crystallizes in triclinic P1 space group and the lattice parameters are shown in Table 1. There are slight variations in the lattice parameters and cell volume of the pure and doped crystals. These variations are due to the incorporation of La^{3+} and Nd^{3+} in the LPM crystal lattice.

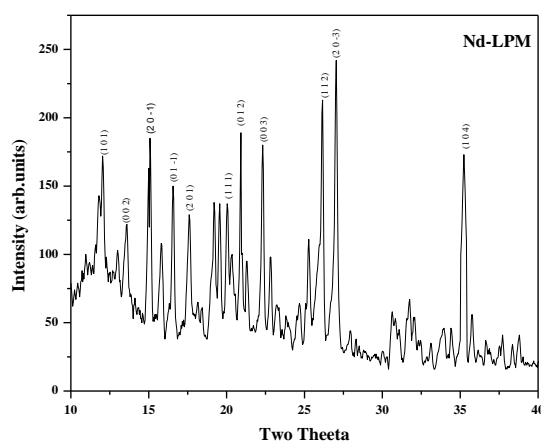***Fig.2*** Photographs of the as grown pure, La-LPM and Nd-LPM crystals
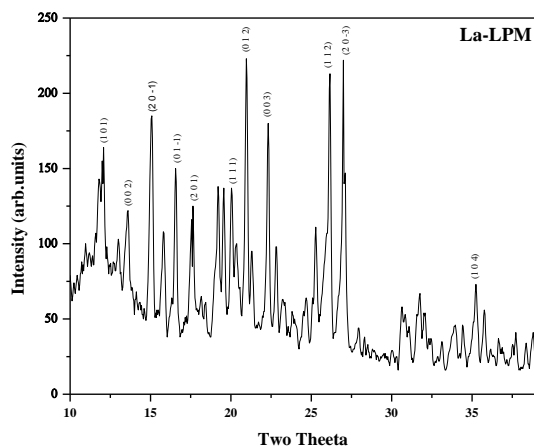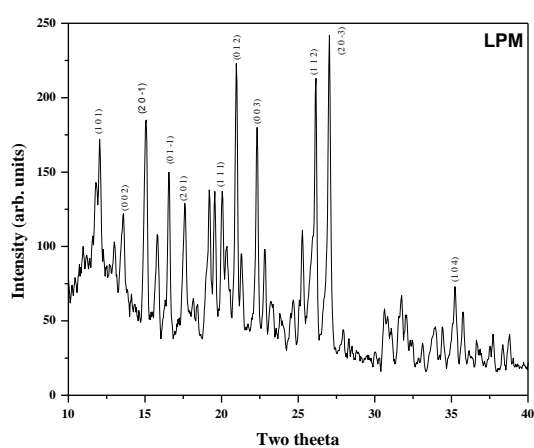
Fig. 3 XRD pattern of Pure and Doped LPM single crystals

Table. 1 Lattice parameter values for the pure and doped LPM

Lattice parameters	Pure LPM	La^{3+}-LPM	Nd^{3+}-LPM
a (Å)	11.101	11.910	11.890
b (Å)	5.410	5.702	5.690
c (Å)	11.510	11.910	11.010
β°	101.1°	100.01	102.10
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space group	P2$_1$	P2$_1$	P2$_1$
Volume (Å^3)	678.32	796.51	728.32

B. Inductively Coupled Plasma studies

The exact weight percentage of the La^{3+}and Nd^{3+} present in doped crystals is determined. 10mg of fine powder of the doped LPM crystals were dissolved in 100ml of triple distilled water respectively, and the prepared solutions were subjected to Inductively Coupled Plasma studies (ICP). The results shows that only 0.7 % of Nd^{3+} and 1.1 % of La^{3+} are present in the respective samples, out of 2 % of the dopant. It is seen that the amount of dopant incorporated in to the doped crystal is less than the concentration of the dopant in the corresponding solution. It is also seen that more La^{3+} ions have gone into the LPM lattice compared to Nd^{3+} ions.

C. UV-Vis-NIR spectra

The optical absorption plays an important role in identifying the potential of the NLO material. Materials having wide absorption window with reduced absorption around the fundamental and second harmonic wavelength are of greater utility for NLO applications. Optical absorption data were taken on these polished crystal samples of about 4 to 6 mm thickness using a Varian carry 5E model dual beam spectrophotometer between 200 – 1200 nm. The spectra (Fig. 4) indicate that the pure and doped LPM crystals have minimum absorption in the entire visible region. The spectra shows that the pure and doped LPM crystals have better lower cut-off wavelengths. Interestingly, both the La^{3+}and Nd^{3+} doped crystals have reduced absorption. The required properties for NLO activity are minimum absorption and low   cut-off wavelength. These properties are improved in the doped crystals [7].
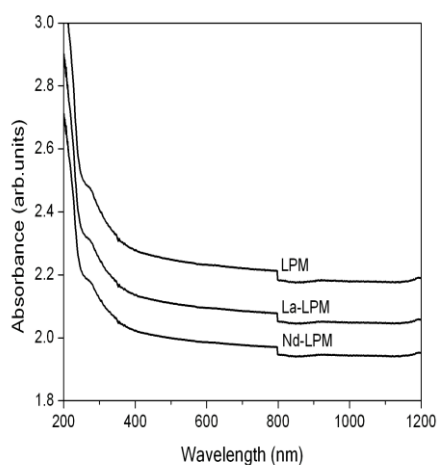
Fig. 4 UV-Vis Spectrum of LPM Pure and Doped

D.   FT-IR Spectra

The FT-IR Spectra of the pure and metal doped LPM were recorded in the range 400 cm^{-1} to 4000 cm^{-1}, using KBr pellet on BRUKKER IFS FT-IR Spectrometer. The FT-IR Spectra of both the pure and doped LPM crystals are shown in Fig 5. The present investigation focuses on the nature and effects of doping Lanthanum and Neodymium into crystal lattices of LPM crystals.   The FT-IR spectra of La doped LPM and Nd doped LPM appear almost similar to that of pure LPM.
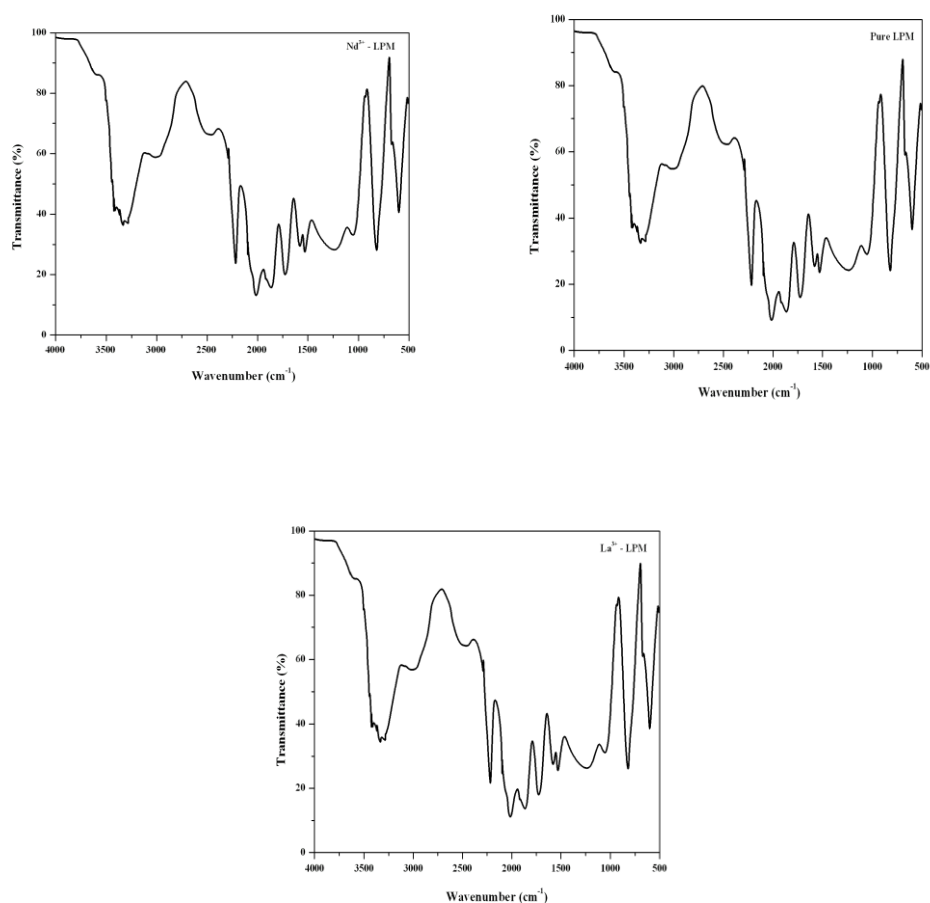

Fig. 5 FT-IR Spectrum of Pure and Doped LPM

O–H 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. The hydroxyl stretching vibrations are generally observed in the region around $3500cm^{-1}$. 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 $3657~cm^{-1}$. Similarly in our case a very strong FT-IR bands at 3905, 3743 and $3684cm^{-1}$ are assigned to O–H stretching vibrations. The hydrogen bonding effect through hydroxyl group leads to dimer conformation OH stretching mode calculated at $3595cm^{-1}$ which is much closer to the FT-IR experimental observation at $3547cm^{-1}$. The O–H in-plane bending vibration in the phenols, in general lies in the region $1150–1250cm^{-1}$ and is not much affected due to hydrogen bonding unlike to stretching and out-of-plane bending frequencies. The weak band in FT-IR spectrum at $1102cm^{-1}$ is assigned to $O_7–H_8$ in plane bending vibration. In our present investigation a strong band observed in FT-IR spectrum at $650~cm^{-1}$ is assigned to O–H out-of-plane bending vibration.

C-N Vibrations

The C-N ring stretching vibration bands occur in the region $1600 - 1500~cm^{-1}$.The present molecule exhibits this vibration in IR spectrum at $1650~cm^{-1}$. C–N stretching absorption assigned in the region $1382–1266~cm^{-1}$. 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. Frequency band observed at $723cm^{-1}$ by theoretical calculation is assigned to C-N out plane bending and band at $600~cm^{-1}$ is due to CN in plane deformation.

C-O Vibrations

The C-O stretching vibration for this LPM molecule is obtained at 1380 and $1230cm^{-1}$ in IR spectrum. 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.

Doping of metal ions into the crystal lattices does not show any significance change in absorption pattern. Some of the absorptions show a marked difference in percentage transmittance. It is inferred that the metal ions (La^{3+} and Nd^{3+}), form weak linkages in the interstices of the corresponding crystals.

E. NLO studies

Kurtz SHG tests were carried out on the pure and doped LPM samples using the Nd:YAG Q-switched laser beam as a source [8]. For a laser input of 6.2mJ, the second harmonic signal (532nm) of 91.66mW, 109.12mW, 193.48mW and 434.39mW were obtained for KDP, pure LPM, La^{3+} and Nd^{3+} doped LPM respectively. Thus, the SHG efficiencies of pure, La^{3+} and Nd^{3+} doped crystals are 1.2, 1.8 and 2.1 times respectively higher that of KDP. Thus, the La^{3+} and Nd^{3+} metals have increased the efficiency of pure LPM.

IV. CONCLUSION

Good quality single crystals of pure, La^{3+} and Nd^{3+} doped L-Phenylalanine Maleate (LPM) were grown successfully by slow evaporation technique. Powder X-ray diffraction studies were carried out, and the lattice parameters are calculated. ICP analysis showed that the amount of dopant incorporated in to the doped crystal is less than the concentration of the dopant in the corresponding solution. The presence of dopant has improved the Nonlinear optical (NLO) properties of the grown crystals and these crystals can be promising material for nonlinear device fabrication.

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