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Growth, Spectral,Thermal, Second and Third-Order Nonlinear Optical Properties on L-Malic Acid Doped Ammonium Dihydrogen Phosphate (ADP) Single Crystals

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ABSTRACT

Ammonium dihydrogen phosphate (ADP) crystals were grown with L-malic acid as an additive in 0.2% molar percentage by slow evaporation method at room temperature. Addition of Amino acid has increased the quality of the crystals and also yields highly transparent defect free crystals. Powder XRD analysis reveals that the crystalline perfection of L-malic acid doped crystals is extremely good without having any internal structural grain boundaries. A Fourier transform infrared (FT-IR) study confirms the functional groups of the crystals. The second harmonic generation efficiency of the crystals was determined by NLO studies. The UV-visible study confirms the wide optical transmittance window for the doped crystals imperative for optoelectronics applications. TG/DTA analyses were carried out to characterize the melting behavior and stability of the title compound. Intensity can be observed from the photoluminescence study. The close and open aperture Z-scan configuration has been used to evaluate the nature of third order nonlinear optical refraction (n2) and absorption (β) for the grown LTADP single crystal.

Keywords: Powder XRD, FTIR, NLO, UV-vis spectroscopy, TG/DTA, Photoluminescence and Z-scan Studies.

I. INTRODUCTION

Crystals are the unacknowledged pillars of advanced technology. Without crystals, there would be no electronic industry, no photonic industry, no fiber optic communications, which depend on materials/crystals such as semiconductors, superconductors, polarizers, transducers, radiation detectors, ultrasonic amplifiers, ferrites, magnetic garnets, solid state lasers, non-linear optics, piezo-electric, electro-optic, acousto-optic, photosensitive, refractory of different grades, crystalline films for microelectronics and computer industries. Crystal growth is an interdisciplinary subject covering physics, chemistry, material science, chemical engineering, metallurgy, crystallography, mineralogy, etc. In the past few decades, there has been a growing interest on crystal growth processes, particularly in view of the increasing demand of materials for technological applications. Single crystals of ADP are used for frequency doubling and frequency tripling of laser systems, optical switches in inertial confinement fusion and acoustic-optical devices [1-5]. ADP has been the subject of a wide variety of investigations over the past decades. Reasonable studies have been done on the growth and properties of pure ADP. In, the present work focuses on L-malic acid as a dopant in ADP and this is expected to enhance the nonlinearity of the crystal. In the last decades, many researchers have tried to found varieties of new NLO materials for laser applications [6]. Nonlinear optical (NLO) materials play a major role in information technology and industrial applications. L-Malic acid doped with ADP will be of special interest as a fundamental building block to develop complex crystal with improved NLO properties. The grown crystals were characterized by PXRD, FTIR, NLO, TG/DTA, UV-vis spectroscopy, photoluminescence and Z-scan Studies.

II. EXPERIMENTAL PROCEDURE

L- Malic acid of 0.3% has been doped with pure ADP (Ammonium dihydrogen phosphate). Calculated quantities of the reactants have been dissolved thoroughly in deionised water. Using magnetic stirrer, the mother solution has been stirred for more than four hours to attain the homogeneous level. The solution has been thoroughly filtered and kept in a dust free environment at room temperature. Optically good transparent defect free crystals have been harvested in a period of 30-35 days and is shown in Figure 1.

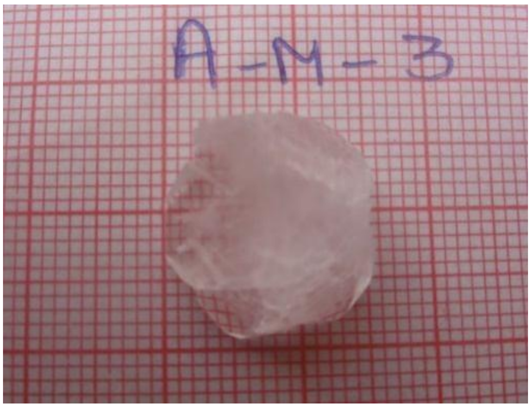

Figure 1. As grown single crystal of LMADP

III. RESULTS AND DISSCUSION

3.1 Powder X-Ray Diffraction Analysis.

X-ray diffraction technique is a powerful tool to analyze the crystalline nature of the materials. Powder X-ray diffraction analysis was carried out by using XPERTPRO X-Ray diffractometer with Cuka radiation (λ=1.5406 Å). The samples were scanned over the range 10-70° as shown in the Fig. 2. The cell parameter values for LMADP are a=b=7.406Å, c=7.526Å with the angles α=β=γ=90° suggested that the LMADP crystal crystallizes in tetragonal structure. The present result is in close agreement with the reported results [7]. The sharp and well-defined peaks at specific 2Θ values indicate the high crystalline nature of the crystal.

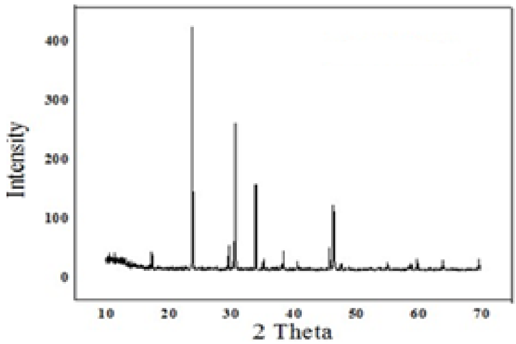

Figure 2. Powder XRD pattern of LMADP crystals

3.2 FT-IR Analysis

FT-IR spectra of LMADP crystal were recorded in range of 450-4000 cm^{-1} by KBr PELLET technique. The functional groups of L-Malic acid doped with ADP crystals have been identified and it was shown in Fig 3. The characteristic peaks of functional groups of LMADP are observed at 3253, 1430,1359, 867 [8]. The broad band in the high energy region is due to the O-H vibration of water, P-O-H group and N-H vibration of ammonia. The peaks at 1325 and 876 cm^{-1} represent PO-H vibrations. The PO_4 vibration gives their peaks at 552and 462 cm^{-1}. The bending vibration of water gives it peak at 1679 cm^{-1} in IR. The peak at 1430cm^{-1} is due to bending vibrations of ammonium. The vibrational band at 3253 cm^{-1} was also assigned to the vibration of N-H band. The C-O stretching mode of vibration and O-H in-plane bending modes of vibration is observed at 1325 cm^{-1} [9]. The PO_4 vibration of the parent is shifted from 552and 462 cm^{-1}, which was confirm by the presence of L-Malic acid on the lattice of ADP crystal.

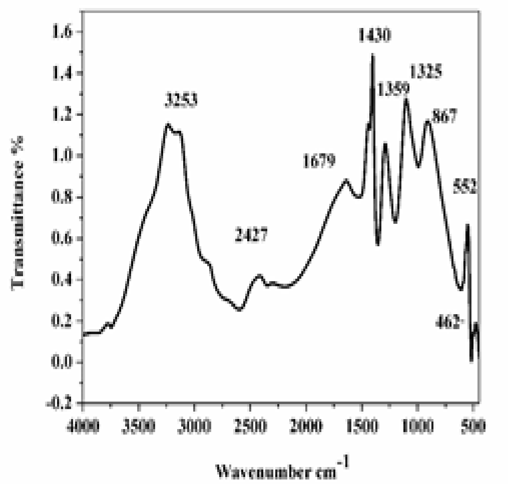

Figure 3. FT-IR Spectral analysis of LMADP crystal

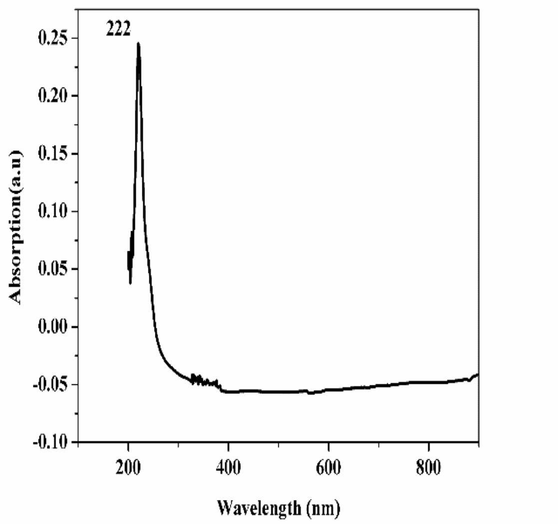

Figure 4. UV-vis absorption of LMADP Crystal

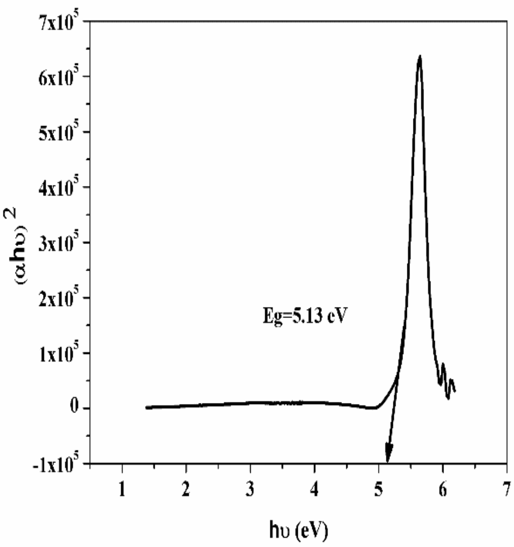

Figure 5. UV-vis band gap of LMADP Crystal.

3.3 SHG Analysis

Kurtz and Perry techniques [10] were employed to measure the SHG efficiency of the grown crystals in reference with the pure KDP. In the measurement, Q-switched Nd: YAG laser of wavelength 1064nm of peak power 2.35 mJ, pulse duration 8 ns and repetition rate 10Hz was used. Output intensity of SHG gives relative values of NLO efficiency of the material. The output energies from the grown sample and reference KDP are found to be 21.2 mW and 19.6 mW respectively. It is found that the SHG efficiency is 1.08 times greater than that of standard KDP.

3.4 Optical Absorption Studies

The UV-Vis spectrum of LMADP crystals were recorded using Perkin Elmer UV-Vis spectrometer (Model: Lambda 35) in the wavelength range of 200-900 nm. Optically polished single crystals of thickness 3mm were used for this study. Fig. 4. shows that the absorption spectrum of the grown crystals and the cut-off wavelength is found to be 222 nm. The presence of lower cut off wavelength and the wide optical transmission window range of the materials possessing NLO activity. The good transmittance property of the crystal in the entire visible region ensures its suitability for second harmonic generation application [11]. The optical band gap energy value is found to be 5.13 eV from Figure 5.

3.5 Thermal Analysis

The thermal behavior of LMADP was studied by the Thermogravimetric (TG) and differential thermal analyses (DTA) recorded using PerkinElmer Diamond TG/DTA instrument. Differential thermogram analysis (DTA) and Thermogravimetric analysis (TGA) give information regarding phase transition and different stages of decomposition of the crystal system. The thermal analyses are used to found out the weight loss (TGA), melting and decomposition point

(DTA) of the grown LMADP single crystal. The DTA curve of LMADP has a major endothermic peak at 213.58^0 C. It coincides with the weight loss in the TGA trace. The endothermic peak at 213.58^0 C represents the melting point of the compound and it was stable up to 188.27°c. Another important observation is that, there is no phase transition and color change till the material melts and this enhances the temperature range for the utility of the crystal for NLO applications. It is observed from the literature that the presence of "higher decomposing temperature doping increases the thermal stability of the compound [12].

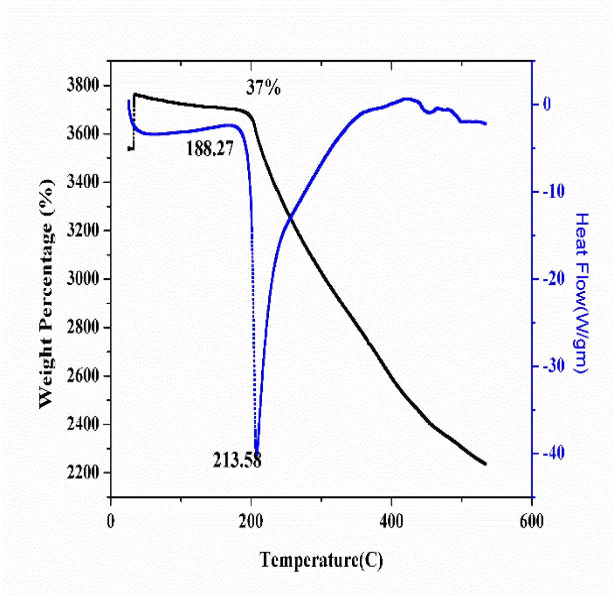

Figure 6. TG-DTA spectrum of LMADP Crystal

3.6 Photoluminescence Studies

The photoluminescence (PL) intensity majorly depends on the excitation energy as well as on the intensity of the incident beam. In present analysis the LMADP crystal has been photo-excited with an excitation wavelength of 363 nm and the EM spectrum was recorded with no delay in the range of 320 to 460 nm. Two emission peaks were observed in the spectrum at 363nm and 423 nm respectively. The results indicate that LMADP single crystal observed violet and blue fluorescence spectrum.

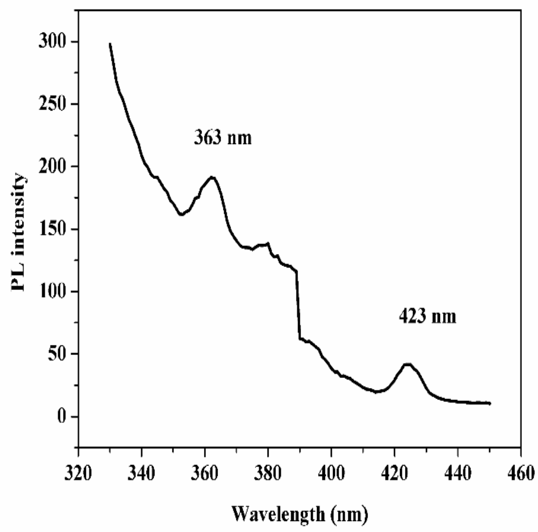

Figure 7. Photoluminescence Emission spectra of LMADP crystal

3.7 Third Order Nonlinear Optical (TONLO) Studies

The single-beam Z-scan is an effective technique to determine the third order nonlinear optical properties of the materials. The simultaneous measurement can be carried using open and closed aperture data to examine the nature of nonlinear index of refraction (n_2) and nonlinear absorption coefficient (β). The study of nonlinear refraction by the Z-scan method depends on the position (Z) of the thin sample which causes focusing and defocussing, depending on whether the nonlinear refraction is positive or negative. Absorption saturation of the sample enhances the peak and decreases the valley in the closed aperture Z-scan. The self-focusing effect (Fig. 5 (a)) is due to the thermal nonlinearity, resulting from the absorption at 632.8 nm. Hence, a spatial distribution of the temperature on the crystal surface produced localized refractive index variations leading to absorption of a tightly focused propagating beam through the LMADP crystal. The details of Z-scan setup are given in Table 1.

Table 1. TONLO parameters of L-Malic acid doped ADP crystal

Parameters and notations	**Details**
Laser beam wavelength (λ)	632.8 nm
Lens focal length (f)	12 cm
Optical path distance (Z)	115 cm
Spot-size diameter in front of the aperture (ω_a)	1cm
Aperture radius (r_a)	4c m
Incident intensity at the focus (Z = 0) (Io)	3.13 MW/cm^2
Sample thickness	2 mm
Effective thickness (L_{eff})	1.8mm
Nonlinear refractive index (n_2)	3. 2* 10^{-12} cm^2/W
Nonlinear absorption coefficient (β)	4.59 *10^{-6} cm/W
Third-order nonlinear susceptibility (χ^3)	2.670*10^{-5} esu

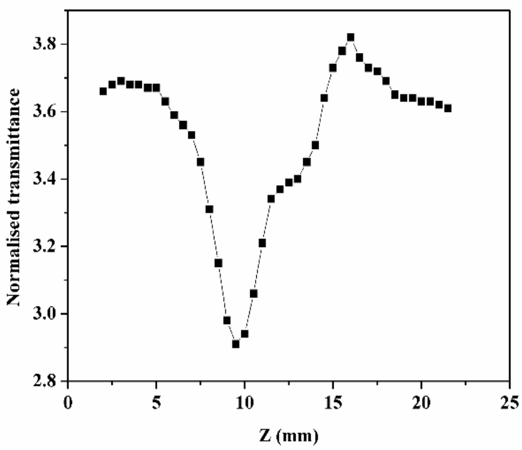

Figure 8. Normalized transmission of closed aperture Z-scan.

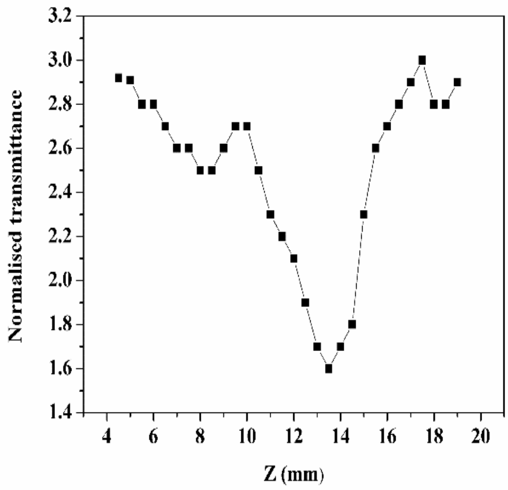

Figure 9. Normalized transmission of open aperture Z-scan.

IV. CONCLUSION

Single crystals of L-Malic acid doped Ammonium Dihydrogen phosphate have been grown by slow evaporation solution growth technique. Transparent crystals of good quality have been harvested within one month. Powder X-Ray Diffraction Analysis (PXRD) revealed the crystalline nature of the grown crystal. The presence of functional groups was confirmed by FT-IR analysis. TGA/DTA confirms that the sample is stable up to 188.27 °C. The result of TGA and DTA analysis pointed out the melting point of the crystal is around 213.58°C. The sharp endothermic peak indicates the high quality of the crystal as well as its perfection. Photoluminescence studies show the excitation of LMADP falls in violet and red fluorescence spectrum. The promising NLO behavior of LMADP crystal has been confirmed by means of SHG efficiency test and Z-scan analysis. The SHG efficiency of LMADP crystal is found tobe1.08 times that of KDP. The third order nonlinear optical susceptibility, nonlinear refractive index and nonlinear absorption coefficient were estimated by Z-scan technique.

V. ACKNOWLEDGEMENT

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