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Investigation on the Linear and Nonlinear Optical Properties of L-Lysine Doped Ammonium Dihydrogen Phosphate Crystal for NLO Applications

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Abstract : *In present investigation L-lysine doped ADP crystal has been grown by slow evaporation technique. The crystalline nature of the grown crystal was confirmed using powder X-ray diffraction technique. The optical studies were carried to examine optical transparency and determine the optical constants of the grown crystal quenching the optoelectronics applications. The optical band gap of grown crystal is found to be 4.7eV. The third order nonlinear behaviour has been investigated using Z-scan technique at 632.8 nm. The nonlinear third order susceptibility of grown crystal is found to be 1 .578 x 10^{-5} esu. The nonlinear index of refraction and absorption coefficient were determined to explore the optical limiting applications of the grown NLO crystal. The kurtz powder test confirmed the second harmonic generations by the grown crystal.*
Keywords: *Growth from solution; UV-Vis; Optical properties; optical susceptibility; SHG efficiency.*

I. Introduction

Nonlinear optical (NLO) frequency conversion materials have a significant impact on laser technology, optical communication and optical storage technology. Ammonium dihydrogen phosphate (ADP) is a potential inorganic material having wide range of applications such as electro-optic modulator, harmonic generators and parametric generators [1-5].

The amino acids are organic materials for NLO application as they have donor carboxylic (COOH) group and the proton acceptor (NH_2) amino group, known as zwitter-ions. Therefore, amino acids can be used as dopants and it was observed that there is enhancement in the material properties such as NLO and ferroelectric properties [6]. L-lysine posses a side chain with hydrogen atom which offers to charge transfer to form semiorganic crystals for nonlinear optical applications [7].

In literature anisotropic studies of L-alanine, glycine, L-arginine and D_L-malik acid doped ADP crystal has been reported [8-10]. The influence of L-lysine monohydrochloride dihydrate on the growth and properties of ADP single crystal have been reported by P. Rajesh et al. [11]. However, no reports on linear and nonlinear properties of L-lysine doped ADP crystal were found. Thus present study reports detailed evaluation of optical properties (optical band gap, extinction coefficient, refractive index, optical conductivity) and third order nonlinear coefficients of L-lysine doped ADP crystal for possible application in optical limiting devices.

II. Experimental Procedure

The AR grade ADP salt was dissolved in deionised water with constant stirring to achieve the supersaturated solution. The saturated solution of ADP was added with 1, 2 and 3 mole percent of L-lysine separately. The L-lysine added solutions were allowed to stir at constant speed to achieve the homogeneity throughout the volume. The Prepared solutions were then filtered and the purity of the salts was achieved by repetitive recrystallization, good quality transparent seed crystals were harvested within 5-6 days by slow evaporation method at room temperature. The Synthesized salts of 1, 2 and 3 mole% L-lysine doped ADP were subjected to SHG test, and it was observed that the 2 mole% L-lysine doped ADP crystal exhibited more SHG efficiency as compare to 1 & 3 mole % and hence of 2 mole% L-lysine doped ADP crystal was grown by slow evaporation technique. The grown crystal is shown in Fig 1.

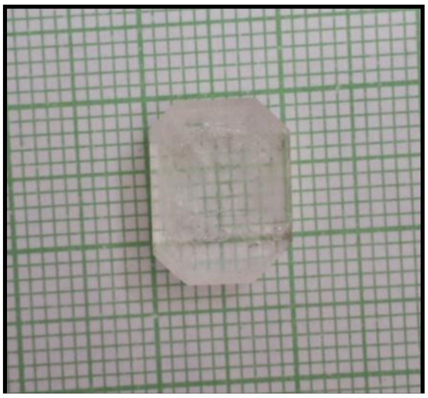

Fig 1. Photograph of the 2 mole% L-lysine doped ADP crystal

III. Results And Discussion

3.1. X-ray Diffraction Analysis

The grown crystal was subjected to powder XRD and the pattern is shown in Fig 2, the unit cell parameters obtained are a=b=7.504 A^0 and c=7.588 A^0 $\alpha=\beta=\gamma=90^0$. The obtained lattice parameter values are in good agreement with literature [11].

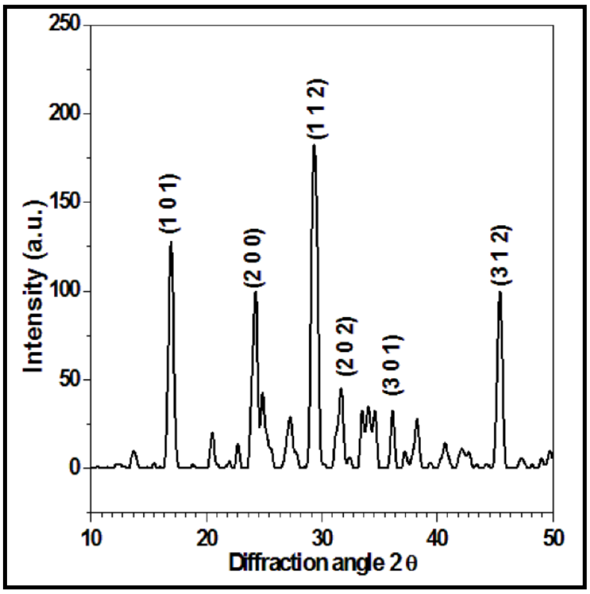

Fig 2. Indexed pattern of doped ADP

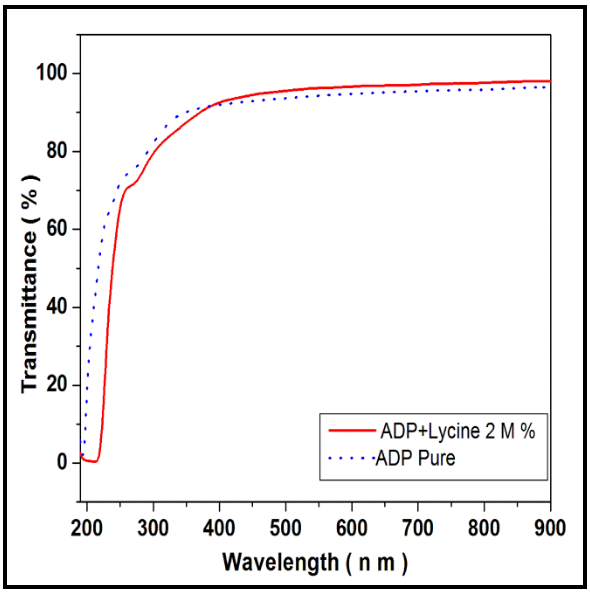

Fig 3. UV-Vis. Transmittance Spectrum

3.2 NLO STUDIES

The second harmonic generation of the grown crystals was examined using the Kurtz and Perry powder technique [12]. The salts of 1,2 and 3mole percent L-lysine doped ADP were subjected to SHG test at IISC, Bangalore, The wavelength 1064 nm from a Q-switched Nd: YAG laser with a pulse energy 2.8mJ/pulse, pulse width 8 ns, and repetition rate of 10 Hz was used. The collected green emission from the powdered sample at the output confirmed the nonlinear behavior of 1, 2 and 3 mole % L-lysine doped ADP crystal. But the 2 mole% L-lysine doped ADP crystal has high output as compare to 1 & 3 mole % L-lysine doped ADP.

3.3 OPTICAL STUDIES

The UV-Visible spectral study of 2 mole % L-lysine doped ADP crystal was carried out using Shimadzu UV-2450 Spectrophotometer in the range 200-900 nm and the recorded transmittance is shown in Fig 3. The grown crystal exhibits high transmittance above 85% in entire visible region. The lower cutoff wavelength is found to be 260 nm indicating the wide optical transmission window favorable for second harmonic generation [13]. The dependence of the optical absorption coefficient (α) on the photon energy (hν) used to study the band structure and the types of transitions of electrons. The electronic band transitions can be well understood from the plot of $(\alpha h\nu)^2$ verses photon energy as depicted in Fig 4. The wide optical band gap of doped ADP crystal is found to be 4.7 eV suggesting its suitability for optoelectronics applications [14].

The variations of extinction coefficient, refractive index are sequentially shown in Fig 5& 6. The least absorption and significantly lower index of refraction in entire visible region exhibited by doped ADP crystal is most desirable property for antireflection coating in solar thermal devices [15]. The plot of optical conductivity against the photon energy is shown in Fig 7. The higher photonic response of optical conductivity and low extinction coefficient is of vital importance for applications in information processing and computing devices. Thus doped ADP crystal is prominent material for NLO applications [15].

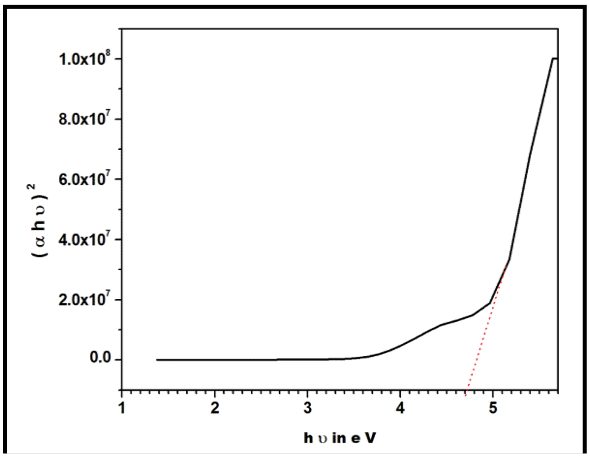

Fig.4 $(\alpha h\upsilon)^2$ **vs. photon energy (hν)**

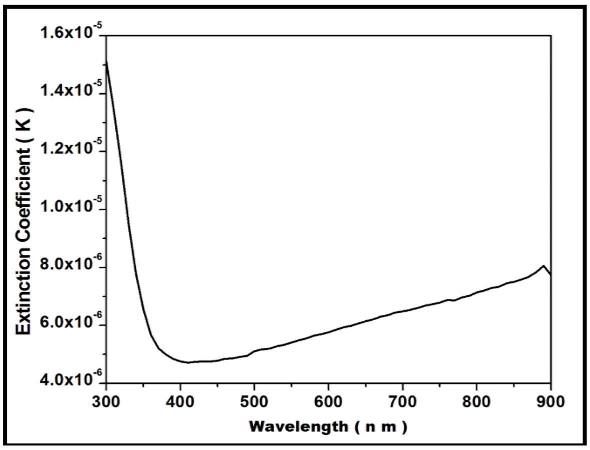

Fig 5. Extinction coefficient vs. Wavelength

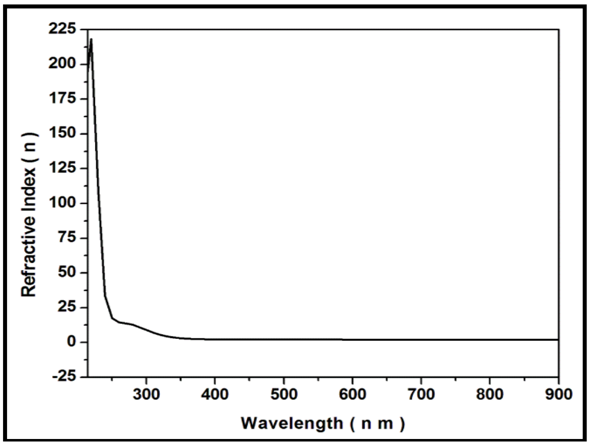

Fig 6. Refractive index vs. wavelength

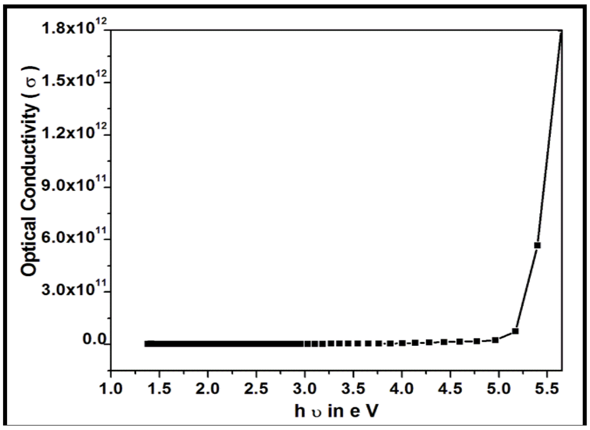

Fig 7. Optical conductivity vs. Photon Energy

3.4 Z-SCAN STUDIES

The single-beam Z-scan is a well-known technique to evaluate the third order nonlinear optical properties of the materials. It allows the simultaneous measurement of both the nonlinear refractive index and nonlinear absorption coefficient. The study of nonlinear refraction by the Z-scan method is based on the intensity dependence of the crystal along a focused Gaussian laser beam. The positive nonlinear refraction or the defocusing due to a negative refraction can be studied using closed aperture transmittance data [16]. A Gaussian beam is focused by a spherical lens onto the sample using a lens of focal length 21.5 cm placed at a far field. The sample is moved along the Z direction and by monitoring the transmittance variation through a small aperture placed at the far field position. The open aperture transmittance data was recorded to determine the nonlinear absorption coefficient of the material. The difference between the peak and valley transmission (ΔTp-v) is written in terms of the on axis phase shift at the focus as,

$$\Delta T_{p-v} = 0.406(1-S)^{0.25}\left|\Delta\phi\right| \qquad (1)$$

where S is the aperture linear transmittance and is calculated using the relation

$$S = 1-\exp(-2r_a^{\,2} / \omega_a^{\,2}) \qquad (2)$$

where r_a is the aperture and ω_a is the beam radius at the aperture. The nonlinear refractive index is given by

$$n_2 = \frac{\Delta\phi}{KI_0L_{eff}} \qquad (3)$$

Where K = 2π / λ (λ is the laser wavelength), I_0 is the intensity of the laser beam at the focus (Z=0),

L_{eff} = [1- exp (-αL)]/ α is the effective thickness of the sample, α is the linear absorption and L is the thickness of the sample.
From the open aperture Z-scan data, the nonlinear absorption coefficient is estimated as

$$\beta = \frac{2\sqrt{2}\Delta T}{I_0 L_{eff}} \quad (4)$$

where ΔT is the one valley value at the open aperture Z-scan curve. The value of β will be negative for saturable absorption and positive for two photon absorption. The real and imaginary parts of the third order nonlinear optical susceptibility χ (3) are defined as

$$\operatorname{Re}\chi^{(3)}(esu) = 10^{-4}(\varepsilon_0 C^2 n_0^{\,2} n_2)/\pi(cm^2/W) \quad (5)$$

$$\operatorname{Im}\chi^{(3)}(esu) = 10^{-2}(\varepsilon_0 C^2 n_0^{\,2}\lambda\beta)/4\pi^2(cm/W) \quad (6)$$

where ε_0 is the vacuum permittivity, n_0 is the linear refractive index of the sample and c is the velocity of light in vacuum.

Table 1.Measurement details and the results of the Z-scan technique

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)	1 cm
Aperture radius (r_a)	4 mm
Incident intensity at the focus (Z=0)	3.13 MW/Cm^2
Effective thickness L_{eff}	1.804 mm
Linear absorption coefficient	1.103
Nonlinear refractive index (n_2)	- 2.68 x10^{-13}cm /W
Nonlinear absorption coefficient (β)	4.063 x 10^{-6} cm/W
Third-order nonlinear optical susceptibility (χ^3)	1.578 x 10^{-5} esu

Thus, we can easily obtain the absolute value of χ^3 by the following formula

$$\chi^3 = \sqrt{(\operatorname{Re}\chi^3)^2 + (\operatorname{Im}\chi^3)^2} \text{ esu} \quad (7)$$

The closed aperture transmittance data depicted in Fig 8 confirms the self defocusing nature as prefocal transmittance peak is followed by the postfocal transmittance valley, indicating negative index of refraction. The negative index of refraction of doped ADP crystal makes it prominent material for protection optical night vision sensor devices [17]. The nonlinear refractive index is found to be - 2.68 x10^{-13} cm /W. The open aperture transmittance data confirmed the saturable absorption by the doped ADP crystal depicted in Fig 9. The open aperture transmittance data was employed to evaluate the nonlinear absorption coefficient (β) of the grown crystal. The effective β value of doped ADP crystal is found to be 4.063 x 10^{-6} cm/W which is relatively lower than potential NLO material [18]. The nonlinear third order susceptibility of grown crystal is found to be 1.578 x 10^{-5}esu which is notably greater than reported crystals [19]. The figure of merit (FOM) can be evaluated using the relation (βλ/n_2). The FOM value of grown crystal is found to be 0.0959 indicating its suitability for photonics applications [19]. The promising third order NLO properties of doped ADP crystals are discussed in Table 1, suggesting its suitability for applications in optical limiting and photonics devices.

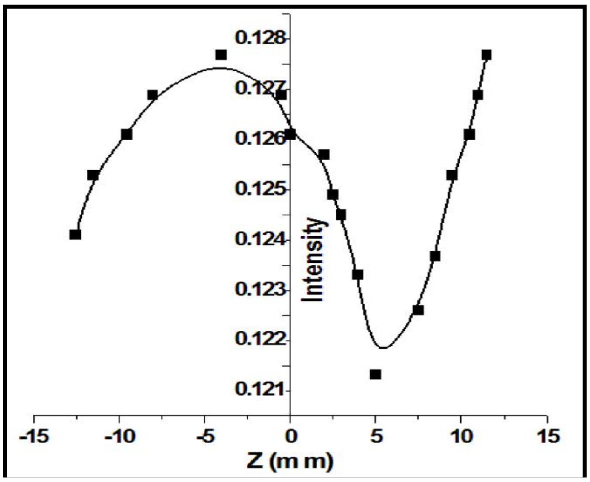

Fig 8. Closed aperture Z-Scan curve

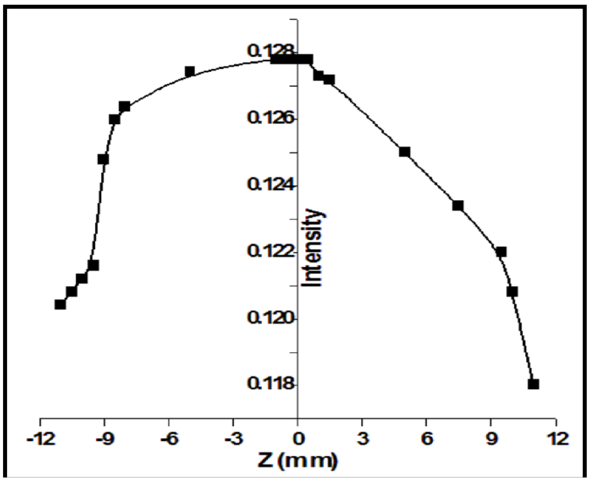

Fig 9. Open aperture Z-Scan curve

IV. Conclusions

The L-lysine doped ADP crystal has been grown from aqueous solution by slow evaporation technique at room temperature. The kurtz powder test confirmed the second harmonic generation of the grown crystal. The optical studies showed wide optical transparency window and enhanced optical constants essential for optoelectronics applications. The optical band gap was found to be 4.7 eV. The negative refractive index ascertained the self-defocusing nature, which is prerequisite property for optical limiting application. The significantly lower nonlinear absorption, FOM value and higher third order susceptibility of grown crystal makes it promising material for integrated NLO applications.

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