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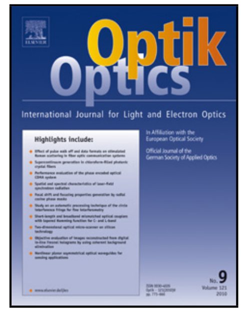

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Emphasized analysis on linear and laser induced nonlinear optical traits of citrulline doped $NH_4H_2PO_4$ (ADP) crystal

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Abstract

The current investigation is aimed to explore the optical studies of citrulline doped ammonium dihydrogen phosphate (ADP) crystal by employing crystal growth, structural, UV-visible, Kurtz-Perry test and Z-scan characterization techniques. The growth of citrulline doped ADP single crystal has been achieved by slow solvent evaporation technique at ambient temperature. The grown crystals have been subjected to single crystal X-ray diffraction technique for structural analysis. The functional groups of grown crystal have been qualitatively identified by means of Fourier transform Infrared analysis. The influence of citrulline on optical transmittance of ADP crystal has been evaluated within 200-900 nm by means of UV-visible spectral analysis. The enhanced second harmonic generation (SHG) efficiency of citrulline doped ADP crystal has been determined using the Q-switched mode Nd:YAG laser and it is found to be 2.18 times higher than standard KDP crystal. The third order nonlinear optical (TONLO) behavior of citrulline doped ADP crystal has been investigated using He-Ne laser operating at 632.8 nm. The close and open aperture Z-scan configuration has been used to evaluate the nature of TONLO refraction (n_2) and absorption (β). The magnitude of TONLO parameters of citrulline doped ADP crystal has been determined using the Z-scan transmittance data. The potential liability of citrulline doped ADP crystal for optical applications has been discussed.

Keywords: Crystal growth; Optical studies; Nonlinear optical materials; X-ray diffraction

1. Introduction

$NH_4H_2PO_4$ (ADP) is an interesting ferroelectric and electro-optic crystal that holds an extended umbrella of

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parametric generators, transducers, electro-optic modulators and many more [1-4]. As identified nonlinear optical (NLO) crystal, ADP crystal offers excellent second harmonic generation (SHG) efficiency having the d_{36} coefficient 1.38×10^{-9} esu [5]. It is exciting fact that in very short span of time ADP has gained much attention and eventually subjected to rigorous investigations for further development as trailed in available literature. The researchers exploring the growth of single/bulk crystal by different techniques [6-7] and by doping selected additives [9] shed more light on the developments that have been achieved in recent past in case of ADP crystal. The literature survey reveals that the modus operandi of doping an organic additive is most influential approach in order to achieve higher enhancement in characteristic properties of ADP crystal. Thereby the doping of several amino acids namely L-valine [10], L-asparginine [11], L-lysine [12], glycine [13-14], L-alanine [15], L-arginene [16], L-proline [17], L-cysteine [18] in ADP crystal has been extensively studied. The results revealed that the performance of amino acid doped ADP crystal capitalizes the undoped ADP crystal in terms of linear and nonlinear optical properties. In addition authors want to notify that our research group is the first to report the doping of L-citrulline in ADP crystal and uncover its effect on optical properties. These factors encouraged our research group to investigate the doping effect of l-citrulline on linear and nonlinear properties of ADP crystal and explore its importance for distinct NLO device applications.

2. Experimental procedure

The AR grade ADP salt was dissolved in double distilled water with constant stirring to achieve the supersaturated solution. The saturated solution of ADP was added with 0.2 mole percent of L-citrulline separately. The mixture was allowed to stir with constant speed for eight hours to avoid co-precipitation at different stages and procure the homogeneous solution. The solution was gradually filtered using No.1whatman filter paper in a clean rinsed beaker and the solution was later kept for slow evaporation at room temperature. The 0.2 mole percent of L-citrulline doped ADP crystal was grown by slow evaporation technique. The as grown citrulline doped ADP crystal is shown in Fig. 1a.

3. Results and discussion

The structural analysis of pure and citrulline doped ADP crystal has been performed by means of single crystal X-ray diffraction (XRD) technique. The structural details were experimentally determined at room temperature using the Enraf Nonius CAD4 single crystal X-ray diffractometer. The XRD data comprised in table 1 reveals that the pure and citrulline doped ADP crystal belongs to tetragonal crystal system with I42d space group. It is noticeable that the unit cell parameters of ADP crystal show slight modification when doped with citrulline. This might have been evolved due to the effective strain developed by dopant on lattice of ADP crystal.

The Fourier transform infrared (FTIR) transmittance spectrum of citrulline doped ADP crystal shown in Fig. 1b has been recorded in the range of 500-4000 cm^{-1} using the Bruker α-ATR spectrophotometer. The presence of functional groups evidenced at different wavenumber has been evaluated to confirm the incorporation of citrulline in ADP crystal matrix. The absorption attributed at 544 cm^{-1} is attributed by C=O rocking vibrations of dopant citrulline. The C-O-H bending vibration associated with citrulline is contributed at 675 cm^{-1}. The P-bond stretching vibration is evident at 922 cm^{-1}. The absorption peak observed at 1527 cm^{-1} is associated with the C-C-N bending vibration. The vibration of characteristic C=O bond is observed at 1695 cm^{-1} is attributed to the. The O-H bond stretching vibration associated with phosphate group is evident at 2344 cm-1. The O-H bond stretching vibration is contributed at wavenumber 3618 cm^{-1}, 3744 cm^{-1}, 3838 cm^{-1}.

Linear optical transmittance in crystal is governed by the electronic transition relying on the absorption of incident photon of specific energy subject to light-matter interaction. The other factors that affects the transmittance of crystal are (a) crystal orientation [19], (b) optically involved functional groups [20] and (c) scattering/absorption by associated defects centers (impurities, voids, inclusions, striations, grain boundaries) [21-22]. In present analysis the optical transmittance of undoped and citrulline doped ADP crystals of 2 mm thickness has been ascertained in the range of 200-900 nm using the Shimadzu UV-2450 spectrophotometer and the traced optical spectrum is shown in Fig. 2a. The observation of spectrum reveals that the ADP crystal has the transmittance of 80% and citrulline doped ADP crystal has transmittance of 89% in entire visible region. The addition of amino acid with wide bonding network favors optical homogeneity and strengthens the crystal structure by minimizing the defect density. In case of citrulline doped ADP crystal the enhancement in transmittance might have been attributed by minimized scattering/absorption of light from defect centers, similar results are evident in many amino acid doped crystals [23-25]. The citrulline doped ADP crystal with high optical transmittance might find huge applications in designing devices utilized in frequency conversion and other parametric processes [26-27].

The material lacking uniform molecular orientation in structural design facilitates origin of significant frequency doubling phenomenon which enables its utility for SHG device applications. Therefore, in current investigation the standard Kurtz-Perry powder test [28] has been employed to determine the SHG efficiency of grown crystals. The good quality single crystals were selected and powdered to micro-granules of uniform size. The powdered sample of each crystal was tightly packed in the quartz cavity and placed at the sample holder position. In order to begin the analysis the Gaussian filtered beam of Q-switched mode operated Nd:YAG laser (1064 nm, 6 ns, 10 Hz) was made incident on each sample and the respective intensity offered by the sample was collected through the optical fiber attached to the spectrophotometer (Black BS Stellernet). The observed green emission confirmed the second order NLO behavior and the intensity dependent SHG response is shown in Fig. 2b. It reveals that the SHG efficiency of citrulline doped ADP crystal is much higher relative to standard KDP crystal material which is 2.18 times higher than the KDP crystal. The SHG efficiency is comparable to the citrulline doped KDP crystal which is 2.2 times higher than KDP crystal material [29]. The SHG efficiency of citrulline doped ADP crystal is systematically compared in table 2. The citrulline doped KDP crystal could be suitable candidate for fabricating frequency convertor devices [30].

The optical nonlinearities originating at high power laser intensities is the most discussed topic that possesses huge demand for manufacturing ultrafast optical processing devices. In present investigation the third order nonlinear optical (TONLO) effects attributed by the grown crystal has been investigated employing the sensitive Z-scan technique developed by Bahae et al [31]. The grown crystal is well polished to 0.5 mm thickness and placed at the focus (Z=0) position of the optical distance reaching to photo-detector. The Z-scan system was initially configured to close aperture and the Gaussian filtered beam was focused on the crystal surface. The crystal sample was translated along the complete Z-direction ranging from -15 mm to 15 mm and the transmitted intensity with reference to position was traced using the photo detector place at far field. The closed aperture Z-scan transmittance of citrulline doped ADP crystal is shown in Fig. 2c. It is observed that the grown crystal attributes the pre-focus peak to post-focus valley evidencing the signature of negative optical nonlinear refraction [32]. The occurrence of negative refraction indicates that the grown crystal belongs to the category of self-defocusing materials significant for optical sensing devices [33]. The phase shift from peak to valley depicts that the irradiation laser beam facilitates the spacial distribution of optical energy giving rise to thermal lensing effect [34-35]. The $\Delta\Phi$ (on axis phase shift) can be derived in terms of ΔT_{p-v} (peak to valley transmittance difference) as [31],

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

where S = [1-exp $(-2r_a^2/\omega_a^2)$] is the aperture linear transmittance, r_a is the aperture radius and ω_a is the beam radius at the aperture. The magnitude of nonlinear refractive index (n_2) was calculated using the relation [31],

$$n_2 = \frac{\Delta\phi}{KI_0L_{eff}} \quad (2)$$

where K = $2\pi / \lambda$ (λ is the laser wavelength), I_0 is the intensity of the laser beam at the focus (Z=0), L_{eff} = [1-exp $(-\alpha L)]/\alpha$, is the effective thickness of the sample depending on linear absorption coefficient (α) and L thickness of the sample. The n_2 of citrulline doped ADP crystal is thus found to be of order of 10^{-15} cm^2/W. The TONLO absorption coefficient (β) has been measured from the open aperture Z-scan configuration. The open aperture Z-scan transmittance curve of grown crystal is Fig. 2d. It reveals that the crystal offers maximum transmittance at the focus position depicting the presence of saturable absorption (SA) phenomenon [36]. The SA effect is dwelled due to dominance of ground state linear absorption coefficient over the excited state absorption [37]. The β value of each crystal has been evaluated using the equation [31],

$$\beta = \frac{2\sqrt{2}\Delta T}{I_0L_{eff}} \quad (3)$$

where ΔT is the one valley value at the open aperture Z-scan curve. The grown crystal offers the β of order 10^{-4} cm/W. The susceptibility in the material assists the polarization to be more effective at high power laser intensities. Therefore, the TONLO susceptibility ($\chi^{(3)}$) of grown crystal has been evaluated using the equations below [31],

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

$$\text{Im}\,\chi^{(3)}(esu) = 10^{-2}(\varepsilon_0 C^2 n_0^{\ 2}\lambda\beta)/4\pi^2(cm/W) \qquad (5)$$

$$\chi^{(3)} = \sqrt{(\text{Re}\,\chi^{(3)})^2 + (\text{Im}\,\chi^{(3)})^2} \qquad (6)$$

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. The susceptibility in the crystal is attributed by the extended π-bonding network of the material and the high magnitude of $\chi^{(3)}$ is most needed parameter for achieving high polarizing capability of material [38-40]. The order of $\chi^{(3)}$ of grown crystal is found to be of order 10^{-4} esu. The optical resolution of Z-scan setup is given in table 3 and the magnitude of TONLO parameters of citrulline doped ADP crystal are discussed with literature in table 4.

4. Conclusion

The citrulline doped ADP single crystal of dimension 19×15×04 mm^3 has been successfully grown cry slow solvent evaporation technique. The crystal structure has been ascertained by single crystal XRD analysis while the coordination and incorporation of citrulline in ADP has been confirmed by FTIR analysis. The linear optical studies established the presence of high optical transmittance of citrulline doped ADP crystal within 200-900 nm which is found 9% higher than ADP crystal. The promising NLO behavior of citrulline doped ADP crystal has been confirmed by Kurtz-Perry test and Z-scan analysis. The frequency doubling effect i.e. SHG efficiency of citrulline doped ADP crystal is found to be 2.18 times higher than KDP crystal material. In TONLO studies the physical origin of negative nonlinear refraction and saturable absorption phenomenon expressed at 632.8 nm by citrulline doped ADP crystal has been explained. The magnitude of TONLO refraction, absorption and susceptibility of citrulline doped ADP crystal is found to be 4.61×10^{-15} cm^2/W, 4.11×10^{-4} cm/W, 7.71×10^{-4} esu respectively. All above studies infer that the citrulline doped ADP crystal is potential optical crystal which holds strong candidature for designing various optical devices.

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Figure Caption

Fig. 1. Citrulline doped ADP (a) single crystal and (b) FTIR spectrum

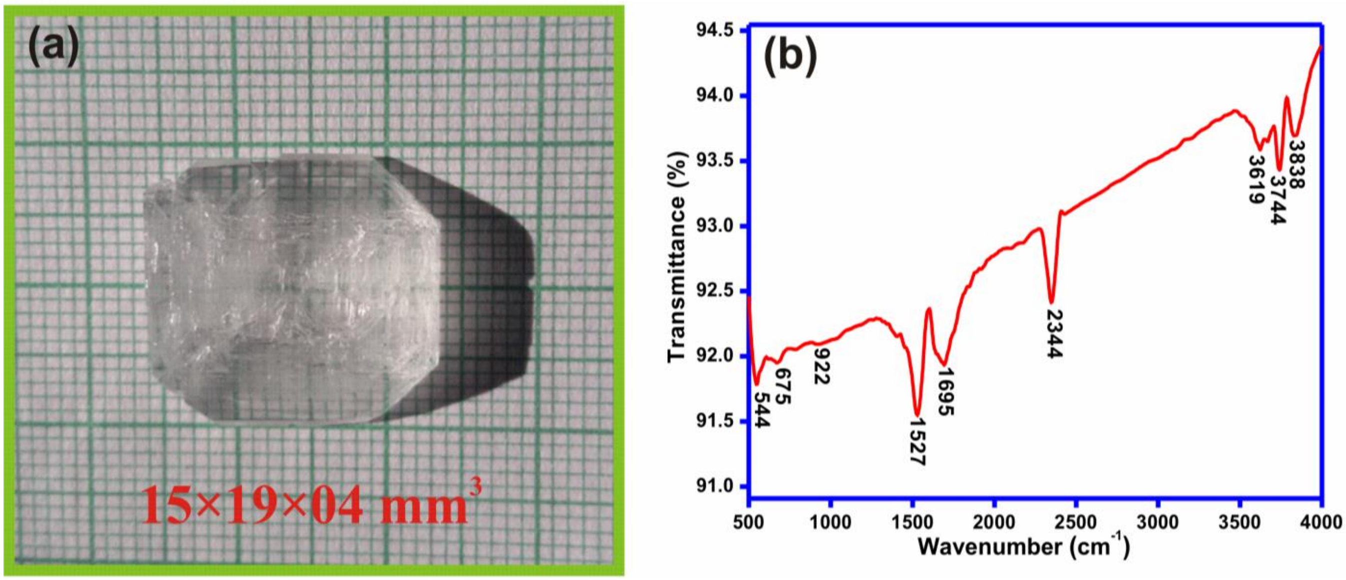

Fig. 2. (a) UV-visible transmittance spectrum (b) SHG response (c) Close aperture Z-scan transmittance curve (d) Open aperture Z-scan transmittance curve

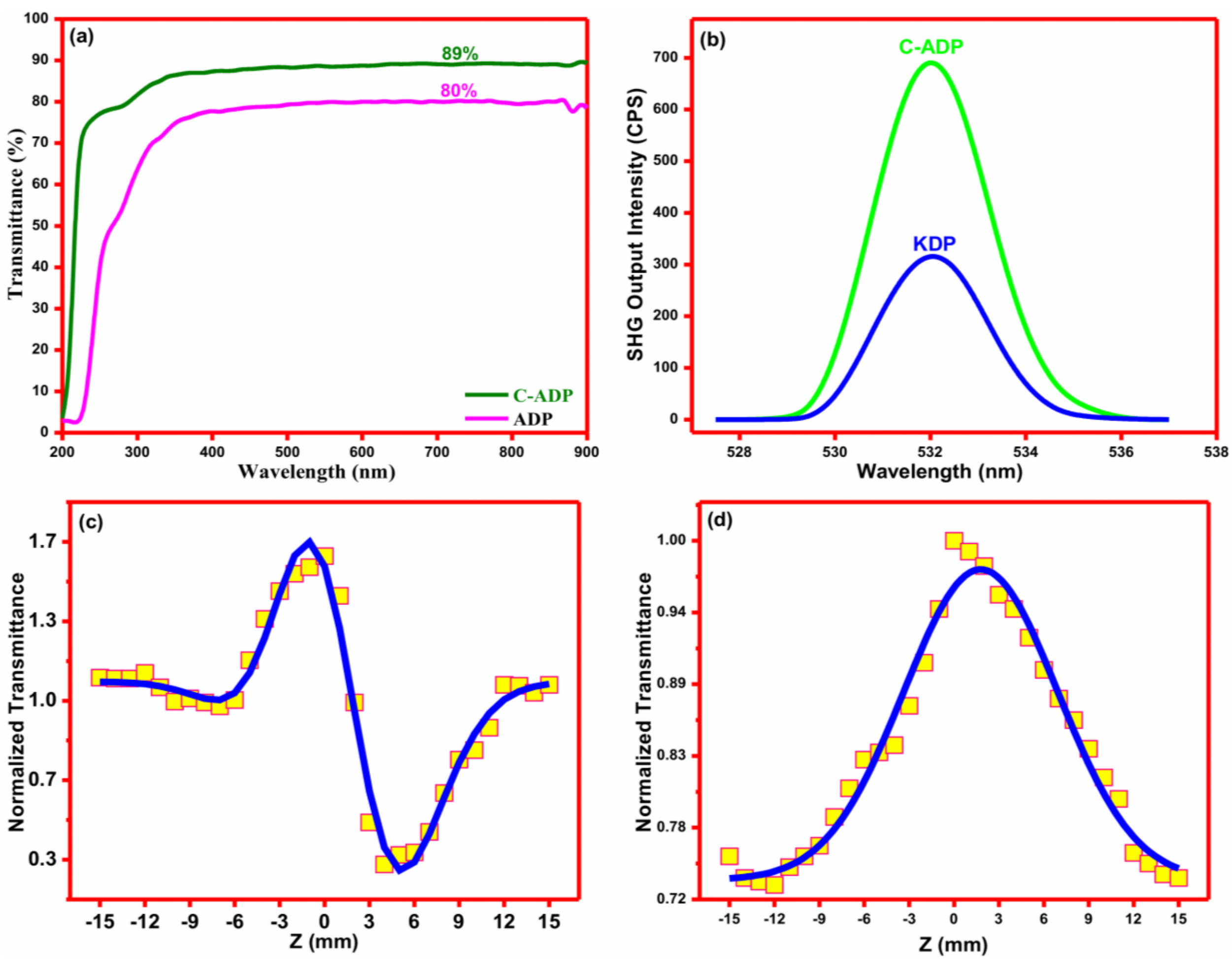

Table 1. Single crystal XRD data

Crystallographic data	ADP	Citrulline doped ADP
Crystal system	Tetragonal	Tetragonal
Space group	I42d	I42d
Cell dimensions (Å)	a=b= 7.52, c= 7.55	a=b= 7.57, c= 7.62
Cell volume $(Å)^3$	426.9	432.4

Table 2. Comparison of SHG efficiency

Dopant in ADP	SHG efficiency	Reference
l-citrulline	2.18 (KDP)	Present study
l-valine	1.92 (KDP)	[10]
l-asparginine	1.1 (ADP)	[11]
Glycine	1.88 (KDP)	[13]
l-alanine	1.8 (KDP)	[15]
l-proline	Value not reported	[17]
l-cysteine	2.05 (KDP)	[18]

Table 3. Z-scan setup details

Parameters	Magnitude
Laser wavelength (λ)	632.8 nm

Lens focal length (f)	30 cm
Optical path distance (Z)	85 cm
Beam waist radius (ω_a)	3.3 mm
Aperture radius (r_a)	2 mm

Table 4. TONLO parameters of amino acid doped ADP crystal

Dopant in ADP	$\chi^{(3)}$ (esu)	n_2 (cm^2/W)	β (cm/W)	Reference
l-citrulline	7.71×10^{-4}	-4.61×10^{-15}	4.11×10^{-4}	Present study
l-valine	4.11×10^{-4}	-4.5×10^{-12}	5.79×10^{-6}	[10]
Glycine	2.249×10^{-6}	4.55×10^{-13}	5.26×10^{-7}	[14]
l-cysteine	1.45×10^{-5}	-5.63×10^{-12}	5.32×10^{-6}	[18]