Studies on L-arginine doped ADP crystals for NLO applications

G. G. MULEY*, M. N. RODE[a], S. A. WAGHULEY, B. H. PAWAR
Department of Physics, Sant Gadge Baba Amravati University, Amravati-444602 (MS) India
[a]*Vaidhyanath College Parli-V, Dist. Beed (MS) India*

Nonlinear optical (NLO) crystals have potential uses in many devices utilizing their ability of frequency conversion, frequency mixing, electro-optic modulation etc. In the present work, single crystal growth and characterizations of NLO L-Arginine doped Ammonium Dihydrogen Phosphate (ADP) from solution by employing slow evaporation of the solvent have been reported. The inclusion of the dopant has been confirmed qualitatively by FT-IR study. UV-VIS-NIR spectroscopy shows the improvement in the optical transparency. Crystal structure has been studied by powder X-Ray diffraction. The Second Harmonic Generation efficiency has been studied by Kurtz and Perry method and found to be **1.22** times more for 2mol% L-Arginine doped ADP as compare to pure ADP. Thermal analysis has also been performed on the grown crystals to study thermal stability.

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1. Introduction

In the view of Nonlinear Optical (NLO) and electro-optical applications, Ammonium Dihydrogen Phosphate (ADP) is firstly studied crystal and still in wide use. It exhibits excellent electro-optical and NLO properties and is commonly used in frequency conversion applications such as second, third and fourth harmonic generation and in electro-optic modulation. ADP is the hydrogen bonded crystal and exhibits important piezoelectric, antiferroelectric, electro-optic and NLO properties. As per doping study concern, the ADP crystal is some what unnoticed. In the present work, an attempt has been made to study the effect of dopant L-Arginine on different properties of ADP. L-Arginine has been selected as a dopant because it is carboxylic acids having an amino group. As L-Arginine contains amine and carboxylic group, it exhibits both acidic as well as basic behaviors and capable of forming hydrogen bonds. It contains *steriocenters (chiral Center)* and thus it is optically active having large Second Harmonic Generation (SHG) efficiency [1-8].

In the present work, single crystal growth of pure and L-Arginine doped ADP from solution has been reported. The FT-IR study was carried out for the qualitative confirmation of inclusion of the dopant in the crystal. L-Arginine doped crystals shows improvement in the optical transparency. The powder X-Ray diffraction study was carried out and calculated lattice parameters have been given in results. The SHG efficiency was found to be 1.22 times more for 2mol% L-Arginine doped ADP crystal as compare to pure crystal.

2. Experimental

2.1 Crystal growth

The ADP salt was dissolved in double distilled water and heated at a 43^{o}C constant temperature with continuous stirring using magnetic stirrer for two hours to obtain a mother solution. The solution was taken in four beakers. In three beakers 2mol%, 4mol% and 6mol% L-Arginine was added and again the solutions were heated at a same constant temperature with constant stirring. The purity of material was achieved by repeated recrystalisation. Four solutions of Pure, 2mol%, 4mol% and 6mol% L-Arginine doped ADP were prepared, filtered and kept in optically heated constant temperature bath of an accuracy ±0.01^{o}C at a temperature 40^{o}C to harvest the seed crystals within 2-3 days. Good quality seed crystals were used to grow good quality single crystals. Photograph of 2mol% and 6mol% L-Arginine doped ADP crystals are shown in Fig.1.

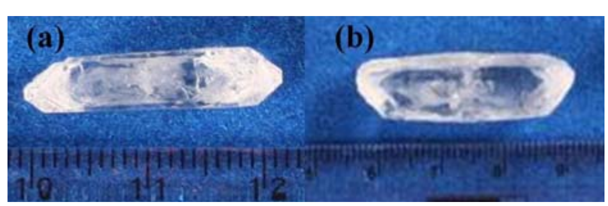

Fig. 1. Photograph of grown (a) 2mol% and (b) 6mol% L-Arginine doped ADP crystals.

2.2 Characterization

The grown crystals were subjected to the FTIR study, SHG efficiency measurement, UV-Visible-NIR study, Powder XRD study and thermal analysis.

3. Results and discussion

3.1 Fourier transform infrared (FT-IR) study

The FT-IR spectra of pure and L-Arginine doped ADP crystals (Fig. 2) were recorded on Perkin Elmer FTIR spectrometer. The absorption peaks observed in the range 3427cm^{-1} to 2405.56cm^{-1} are attributed to the P-OH stretching of H_2PO_4, O-H stretching of COOH and water of crystallization, N-H stretching of NH_3,, C-H stretching of CH_2 and CH. The peaks observed in the range 1751.19cm^{-1} to 1635.34cm^{-1} are attributed to C=O stretching, P–O–H bending and –C=NH_4 stretching. C-H Deformation, C=O and N-H Stretching shows peaks in the range 1401cm^{-1} to 1444.03cm^{-1}. The peaks around 1288 cm^{-1} are considered due to CH_2 bending, O-H Deformation, C-O, C-N, P=O stretching of ADP, and around 1100cm^{-1} due to C-H, O-H Deformation, C-O Stretching. Peaks observed at 1000.5cm^{-1}, 901.96cm^{-1}, 896.17cm^{-1}, 897.701cm^{-1} are attributed to P-OH and C-H stretching and at 757.5cm^{-1}, 697.6cm^{-1} to the HO–P–OH bending[9].

Doped ADP crystals shows more absorption peaks in the FT-IR spectra as compare to pure ADP. The observed extra peaks correspond to be the functional groups of L-Arginine, which confirms the inclusion of the L-Arginine in the ADP host crystals.

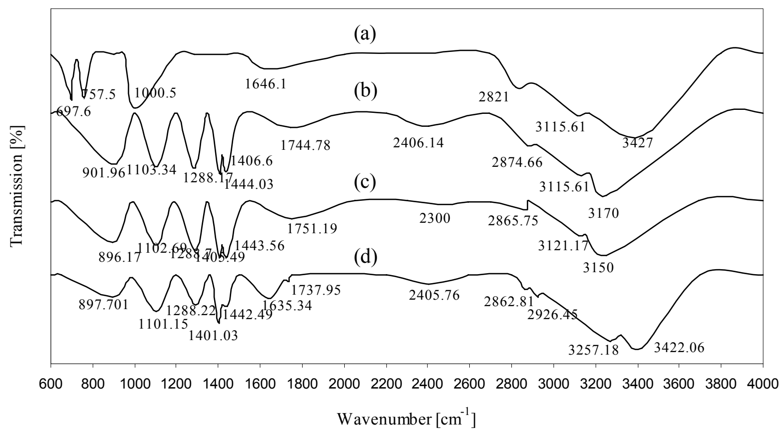

Fig. 2. FT-IR Spectra of (a) Pure, (b) 2mol%, (c) 4mol% and (d) 6mol% L-Arginine doped ADP.

3.2 SHG measurements

SHG efficiency of grown crystals was measured by employing Kurtz and Perry method [10]. In the experiment Q-switched, mode locked Nd: YAG laser of wavelength 1064nm having peak power 2.47mJ, pulse duration 8 ns and repetition rate 10Hz was used. The out put was measured at wavelength 532nm. The SHG efficiency found to be more in doped ADP crystals as compare to the pure crystal. The SHG efficiencies have been shown in Table 1. The increase in the SHG efficiencies are due to the weakening of the bond between O–H and C=O due to hydrogen bonding [6-8].

Table 1. SHG efficiency of pure and L-Arginine ADP.

	Measured out put	SHG efficiency
Pure ADP	383mV	1
2mol% L-Arginine doped ADP	467mV	1.22
4mol% L-Arginine doped ADP	456mV	1.19
6mol% L-Arginine doped ADP	425mV	1.11

3.3 XRD study

The powder X-ray diffraction patterns (Fig. 3) of the pure and 2mol% L-Arginine doped ADP crystals were recorded on X-ray diffractometer XPERT-PRO using Cu Kα radiations (1.54060Å, 40 mA, 45 kV). The powder samples were scanned in steps of 0.0170° for a time interval of 10.3359 sec over a 2θ range of 10.0144–119.9874°. The data has been analyzed and unit cell parameters (Table 2) have been calculated.

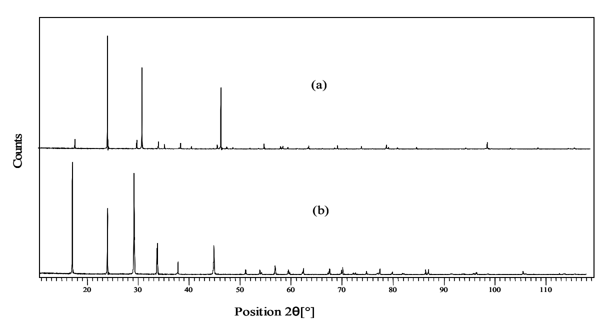

Fig. 3. Powder XRD Pattern of (a) pure and (b) 2mol% L-Arginine doped ADP.

Table 2. Unit cell details.

	Crystal system	Space group	Unit cell parameters
ADP	Tetragonal	I-42d	a=b=7.503Å, c=7.556Å $\alpha=\beta=\gamma=90^0$
2mol% L-Arginine doped ADP	Tetragonal	I-42d	a=b=7.503Å, c=7.557Å $\alpha=\beta=\gamma=90^0$

3.4 UV-visible-NIR spectroscopy

The UV-Visible-NIR spectroscopy was performed on the samples by using UV-1700 SHIMADZU SPECTROPHOTOMETER over the wavelength range 190 nm to 1100 nm.

From the UV-VIS-NIR spectra of pure and L-Arginine doped ADP crystals (Fig. 4) it is clear that the transparency increases with increasing concentrations. The increase in the transparency of the doped ADP crystals with respect to pure ADP at 305nm found to be about 11%, 27.5% and 32.99% for 2mol%, 4mol% and 6mol% L-Arginine doping and at 1100nm it is found to be 2.32%, 5.73% and 6.83%, respectively.

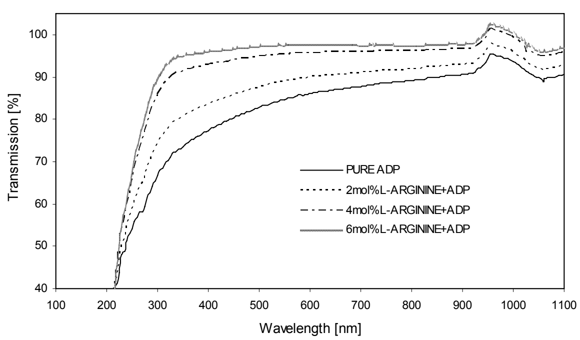

Fig. 4. UV-VIS-NIR spectra of pure and L-Arginine doped ADP.

3.5 Thermal analysis

The thermal analysis of the pure and 2mol% L-Arginine doped ADP crystals was done by recording the TGA curve using Perkin Elmer Dimmer TGDTA at a heating rate of 15°C/min under Argon atmosphere to know the thermal stability of the crystals.

Recorded TGA curve of pure ADP (Fig. 5) shows the maximum 12.77% weight loss in the temperature range 250°C to 347°C, which corresponds to the decomposition of the ADP and liberation of Ammonia and water molecules. Prolonged heating doesn't produce any weight loss up to the end.

The TGA curve of 2mol% L-Arginine doped ADP crystals (Fig. 6) shows a weight loss starting from 78°C and ends at 104.19°C with about total 24% weight loss, which corresponds to the evaporation of water molecule. Second weight loss occurs in the temperature range 259-297°C. In this range 5.31% total weight loss takes place, which may be due to the decomposition of the ADP and L-Arginine.

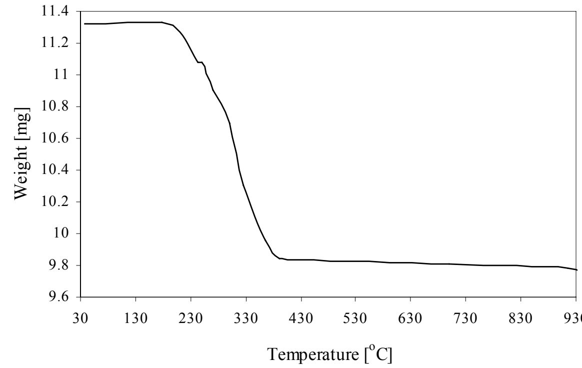

Fig. 5. TGA curve of pure ADP.

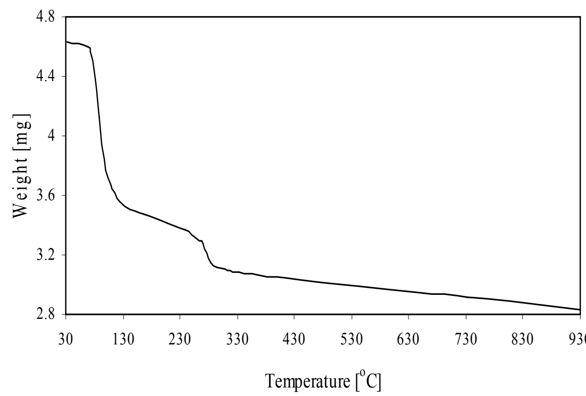

Fig. 6. TGA curve of 2mol% L-Arginine doped ADP.

4. Conclusions

Pure and L-Arginine doped ADP crystals were grown by Solvent Evaporation Solution Growth Method at a 40°C.

FT-IR Spectroscopy of the pure and doped KDP crystals confirms qualitatively the expected inclusion of the L-Arginine in the doped ADP crystals.

Pure and doped ADP crystals crystallize in the same tetragonal crystal system and the calculated lattice parameters of doped ADP crystals deviates slightly from the lattice parameters of pure ADP.

The increasing doping level in the ADP crystal improves optical transparency and also improves the sharp cutoff.

SHG efficiency test confirms the increase in the SHG efficiency in doped ADP crystals. 2mol% doped ADP crystal has **1.22** times more SHG efficiency than pure crystal.

TGA study confirms the thermal stability of the grown crystals.

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*Corresponding author: gajananggm@yahoo.co.in