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Growth and Characterization of Pure and L-Aspartic acid doped ADP Single Crystal

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ABSTRACT

Pure and 0.1 mole % L-aspartic acid doped Ammonium Dihydrogen Phosphate (ADP) have been grown by solvent slow evaporation technique at room temperature. The grown crystals were characterized by powder X-ray diffraction, Uv-visible, FTIR and Raman FTIR analysis. The doping of L-aspartic acid was confirmed by FTIR spectrum and Raman FTIR. The Nonlinear optical property (SHG) of L-aspartic acid doped ADP was increased than the Pure ADP. Thermally stable for both pure and L-aspartic acid doped ADP crystal. Micro hardness studies were carried out on the grown crystal.

Introduction

The wellknown NLO Ammonium Dihydrogen Phosphate crystals have superior properties and it had been exploited for variety of applications. It possessed piezoelectric, dielectric, ferroelectric, nonlinear optical and electro-optic properties. It is used in high-speed modulation and switching of optical signals for telecommunications and signal processing [1-5]. Many researchers processed many studies in metal ion doped crystals [6-8]. Amino acid is an organic material, when it was doped with ADP would be increased its optical properties. In this paper L-aspartic acid was doped with ADP to increase its optical properties.

Experimental procedure

Crystal growth

Pure ADP crystal was grown by Solution growth technique at room temperature. AR grade ADP salt was dissolved in 100 ml Millipore water resistivity 18.2 MΩ cm. The solution was mixed thoroughly using magnetic stirrer about 6 hours. The super saturated ADP solution was filtered using Wattman filter paper and poured in to petri dishes. These petri dishes were covered with paper and kept for slow evaporation. The good transparent crystals were taken after three days and shown in Figure.1. Their average dimensions were 30 mm x 20 mm x 8 mm and they are non hygroscopic in nature.

The super saturated solution of ADP was taken in another 100ml beaker and 0.1 mole% L-aspartic was added. Now this solution was filtered and the same was left for crystallization at room temperature. After four days, the transparent doped crystals were taken after three days and shown in Figure 1. The stochiometric equation of the reaction is given below.

$$NH_4H_2PO_4 + C_4H_7NO_4 = NH_4H_2PO_4 : C_4H_7NO_4$$

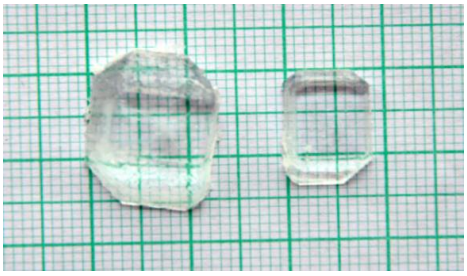

Fig 1. Grown pure and L-aspartic acid doped ADP crystal

Results and Discussions

Powder XRD studies

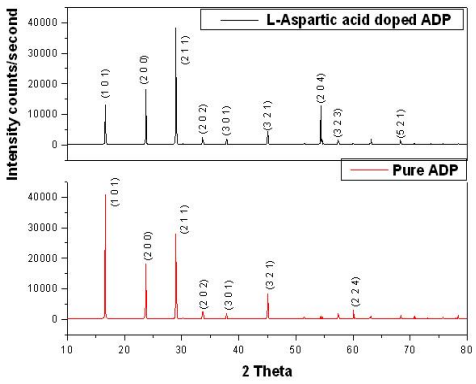

Fig 2. Powder XRD pattern of as grown pure and L-aspartic acid doped ADP crystals

The crystalline nature of the grown pure and L-aspartic acid doped ADP crystal were analyzed by powder x-ray diffraction technique. Well defined Bragg's peak were obtained at specific 2 Theta angles fig 2 conforms the crystalline nature of the grown crystals. The hkl values for prominent peaks were identified and indexed. The additional peaks in L-aspartic acid crystals were conform that the dopent were present in the crystal. Using single crystal x-ray diffraction analysis the Lattice parameters were calculated as a=6.7909Å, b=6.7909Å and c=6.7927Å for doped ADP crystal. The crystallographic angles are 90 degree (α=β=γ = 90°). The volume of the unit cell is 92.25709 Å^3.

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Hence the grown crystals belongs to tetragonal system. Only the volume had changed compared to pure ADP. The dopent might be seated in the interstitial site.

FTIR spectral studies

FT-IR spectrums of pure and L-aspartic acid doped crystals were recorded by **Perkin Elmer FT-IR spectrometer** in the range of 400-4000cm^{-1} using **KBr pellet** technique of resolution 0.9 cm^{-1}. It was a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms in the crystal. The FTIR spectrum for L-aspartic acid doped ADP crystal is as shown in fig.3.

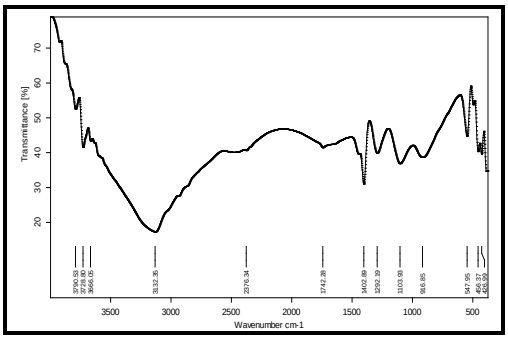

Fig 3. FTIR spectrum for L-aspartic acid doped ADP crystal

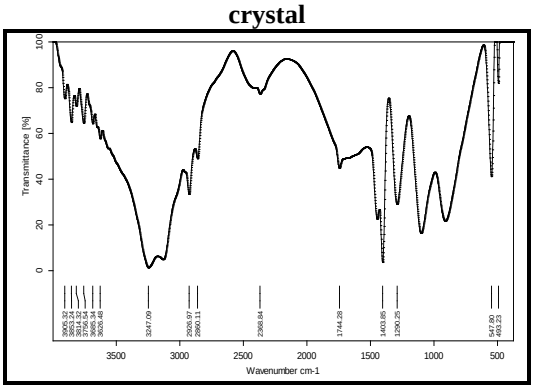

Fig 4. FTIR spectrum for pure ADP crystal.

Figure 4 shows the FTIR spectrum of the pure ADP. The broad band in the high energy region is due to O–H vibrations of water, P–O–H group and N–H vibrations of ammonium (9). The broadness was due to the hydrogen bonding interaction with adjacent molecules (10). The band at 2376cm $^{-1}$ was assigned to hydrogen bond.[11]. The peak at 1403 cm $^{-1}$ was due to bending vibrations of ammonium (10). The very strong band at 1292cm $^{-1}$ was due to the combination of the asymmetric stretching vibration of PO_4 with lattice [12] . The P–O–H vibrations give the peaks at 1103 cm $^{-1}$ and 916 cm $^{-1}$. The PO_4 vibrations give their peaks at 548 cm $^{-1}$ and 457 cm $^{-1}$.

Similar peaks were observed in the FTIR spectrum of L-aspartic acid doped ADP crystals. The additional peaks at 1744, 2860 and 2926 cm^{-1} are due to stretching vibration of CH_2 which confirms the doping of L-Aspartic acid **[10-13]** . It was tabulated in table 1.

FT-Raman Spectral Analysis

FT-Raman Spectroscopy is another tool for identification of functional groups present in the grown crystals. It was a complimentary to the FTIR spectral analysis. The functional groups present in the crystals were confirmed here also. The FT-Raman spectrum of Pure and L-aspartic acid doped ADP crystals as shown in fig.6 and fig.5.

In the FT-Raman spectrum of low-wave number weak peaks appear at 125 cm $^{-1}$ and 177 cm^{-1} in the case of the l-aspartic acid grafted on compound, belonging to the lattice vibration modes of ADP crystal. The former corresponds to the translational mode of NH_4^+ ion, observed at the same frequency [14]. However, the line at 177 cm $^{-1}$ is assigned to the vibration mode of PO_4^{3-} ion, as observed by at 174 cm $^{-1}$[15]. The strongest line at 927 cm $^{-1}$ correspond to the symmetric stretching vibration modes of PO_4^{3-} [16]

Table 1. Frequency assignment of pure and doped ADP crystals

Pure ADP	L-Aspartic acid doped ADP	Assignments
3666	3814	O-H stretching of ADP
	3247	N-H stretch of L-Aspartic acid
	2926	C–H aliphatic stretching superimposed with N–H stretching
	2860	P-O-H symmetric stretching
2376	2368	P-O-H bending of ADP
1724	1744	C=O stretching
1402	1403	NH4 bending of ADP
1292	1290	P=O stretching of ADP
1103		P-O stretching of ADP
916		P-O-H stretching of ADP
547	547	OH-P-OH bending

The Raman bands of the compound around 3000 cm $^{-1}$ are attributed to O–H stretching vibration of the carboxyl group. The medium peak at 1659 cm $^{-1}$ is assigned to the stretching vibration of C=O group. The weak peaks at 1462 cm $^{-1}$ and 1422 cm $^{-1}$ are attributed to the in-plane bending of the amino group. The peaks at 756 cm $^{-1}$, 742 cm $^{-1}$, 561 cm $^{-1}$ and 479 cm^{-1} are mainly due to stretching vibrations of PO_4 [16,17]

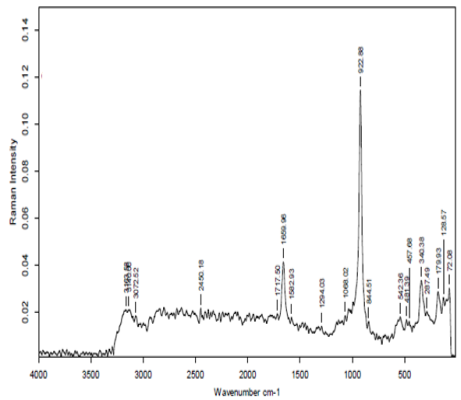

Fig 5. Raman spectrum for L-aspartic acid doped ADP

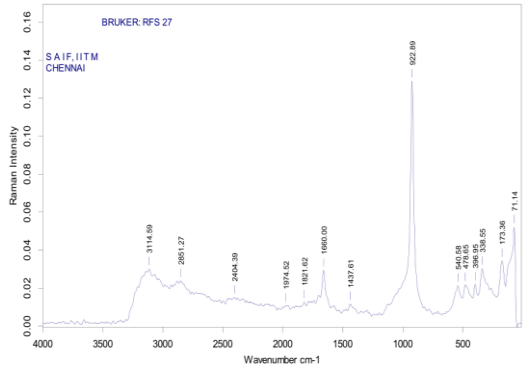

Fig 6. Raman spectrum for Pure ADP

Uv-visible studies

The Uv-visible spectra were recorded for doped and pure ADP crystals. Fig. 7 shows the graph between the transmittance and wavelength. It is observed that doping slightly changes the optical transmission. L-aspartic acid doped ADP optical transmission increases. It is observed that the above crystals have transmittance in the entire visible and near IR region. This

is very important for materials possessing non-linear optical properties. The Uv cut off wave length for pure and doped crystals are found to be at 200nm

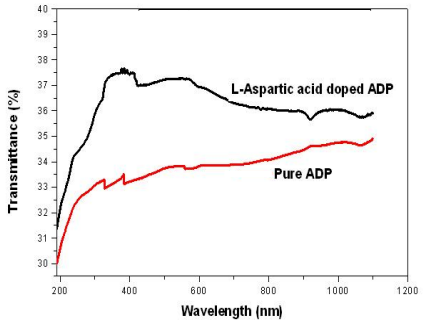

Fig 7. Uv- spectrum of Pure and L-aspartic acid doped ADP crystal

SHG Efficiency measurement

The Second Harmonic generation (SHG) efficiency of the grown crystals were checked using Kurtz and Perry Technique.(6). It is found that the efficiency of L-aspartic acid doped ADP is greater than pure ADP crystals which are tabulated in Table 2.

Table 2. SHG Efficiency of pure and L-aspartic acid doped ADP

S.No.	Sample	SHG signal (mv)	Efficiency with respect fo ADP
1	Pure ADP	9.5	1.00
2	ADP + L-aspartic acid	13	1.36

Micro hardness studies

Hardness is one of the important mechanical properties of the materials. It can be used as a suitable measure for strength of a material. Micro hardness measurements were carried out using Vicker's Micro hardness tester fitted with a diamond indenter. The Well polished doped ADP crystal was placed on the platform of the Vickers Micro hardness tester and the loads of different magnitudes were applied over affixed interval of time. The indentation time was kept as 8s for all the loads. The hardness was calculated using the relation Hv = (1.8544 x P)/(d^2) kg/m^2 , where **P** is applied load in grams and **d** is the diagonal length of indentation.[7-8]. The Hv of various loads of pure and L-aspartic acid doped ADP crystals are shown in Fig 8. The hardness increases gradually with the increase of load and above 100 gram cracks develop on the smooth surface of the crystal due to the release of internal stresses generated locally by indentation. The values are tabulated in Table 3. From the graph, we observed that the micro hardness of L-aspartic acid doped ADP value is more than pure ADP crystal.

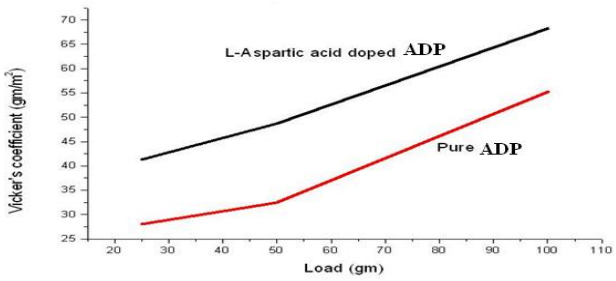

Fig. 8. Vicker's coefficient for Pure and L-aspartic acid doped ADP

Table 3. Vicker's coefficient for Pure and L-aspartic acid doped ADP

S. No.	LOAD in gm	Vicker's Hardness coefficient	
		Pure ADP	L-aspartic acid doped ADP
1	25	25.4	41.25
2	50	32.5	49
3	100	55	68.2

Thermal Analysis

The thermal behavior of the sample was studied by thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) using diamond Perkin Elmer system in the temperature range RT to 900˚C.

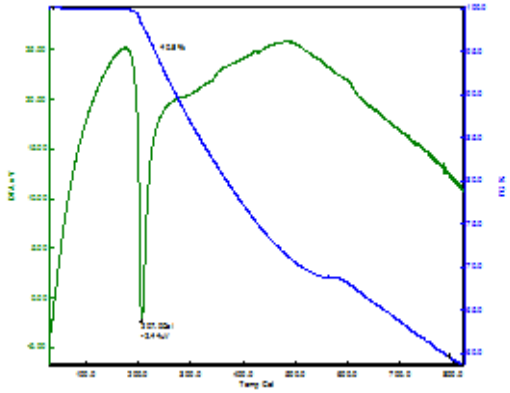

Fig 9. TGA and DTA curves for pure ADP crystal

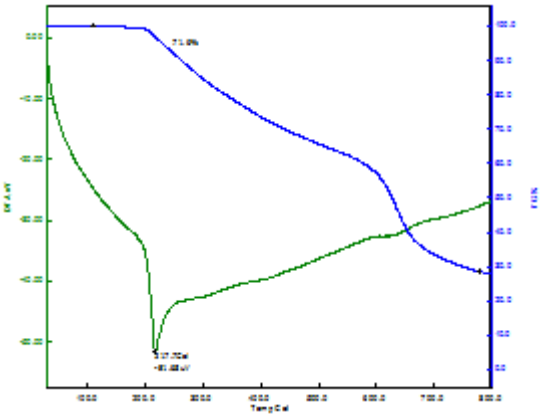

Fig 10. TGA and DTA curves for L-aspartic acid doped ADP crystal

The TGA and DTA curves recorded simultaneously for pure and L-aspartic acid doped ADP crystals are displayed in Fig.9 & 10. The percentage of weight loss of the samples as a function of temperature is measured in TGA. Since there is no weight loss in the temperature ranges 0 - 207˚C, pure and L-aspartic acid doped ADP are thermally stable till 207˚C. The absence of water of crystallization in the molecular structure is indicated by the absence of weight loss around 100˚C. The TGA curve also shows the difference stages of decomposition.

Conclusion

The pure ADP and L-aspartic acid doped ADP crystals were grown successfully using low temperature solution growth technique. The dimension of the grown L-aspartic acid doped ADP crystal was 30 mm x 20 mm x 8 mm. The presence of L-aspartic acid in the crystal lattice of ADP was confirmed by single crystal X-ray diffraction and powder X-ray diffraction. The FT-IR spectrum shows that all the functional group present in pure ADP and L-aspartic acid doped ADP crystals. The cutoff frequency of L-aspartic acid doped ADP crystal was lower than that of pure ADP from the analysis of the UV- vis spectrum. The L-aspartic acid doped ADP crystal has good

transmittance window in the visible and IR region. It was observed that the SHG efficiency of L-aspartic acid doped ADP crystal was conformed. The L-aspartic acid doped ADP crystal was mechanically stronger than pure ADP crystal. Pure and L-aspartic acid doped ADP crystal has no water molecule and thermally stable. Hence L-aspartic acid doped ADP is useful for device application.

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