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Research Article

GROWTH, STRUCTURAL, OPTICAL AND MICROHARDNESS BEHAVIOUR OF PURE AND DELONIX ELATA LEAF EXTRACT DOPED ADP CRYSTALS

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ABSTRACT

Pure and Delonix leaf extract added ammonium dihydrogen phosphate (ADP) single crystals have been grown at room temperature by the slow evaporation method. The grown crystals have been characterized structurally, chemically, thermally, mechanically and optically using the available standard methods. The powder X-ray diffraction and Fourier Transform Infrared Spectral measurements confirm the crystal and molecular structures. Thermogravimetric, UV-Visible spectral and micro hardness measurements indicate respectively the thermal stability, optical transparency and mechanical stability of the grown crystals. Result of the scanning electron microscope indicating the morphology of the pure ADP and doped crystals via, spherical and coarse shape. From the single XRD the lattice parameter values are a= 7.53 Å, b= 7.53 Å, and c= 7.58 Å with angles α= β= γ= 90° belongs to tetragonal structure.

INTRODUCTION

Now-a-days crystals have grown to be pillar of modern science and technology in all the compliments with aspect and always increasing the demand of single crystals in the variety of field. Today with modern technology, using sophisticated instrument several national laboratories and university are growing varieties of crystals, it may be categorized into three major crystal growth processes:

Solid growth → Process involving solid-solid phase transitions.
Melt growth → Process involving liquid-solid phase transitions.
Vapour growth → Process involving gas - solid phase transitions.

However, there are three general categories of crystal growth methods, viz., (i) growth from melt (ii) growth from solution and (iii) growth from vapour, which have the helpfulness in day to day life still the growth of some crystals by using simple equipment by utilizing basic properties of material much of the as research work (Canham, 1990; Sekhar and Ashley, 1991). Now the growth of ADP (Ammonium dihydrogen phosphate) and Delonix elata leaves extract mixed ADP crystals by slow evaporation technique which is one of the simplest techniques have been undertaken in the present work. Ammonium dihydrogen phosphate ($NH_4H_2PO_4$) is a technologically important inorganic material and studies on ADP crystal are a focus for their exceptional piezo-electric, antiferro- electric, electro-optic and dielectric (Kuppurao *et al*, 1997; Dixit *et al*, and Zaitseva *et al*, 2001; Klimentov *et al*, 1994; Ramirez *et al*, 1990; Marde *et al*, 1991). Frequently, applications of the nonlinear optical (NLO) property have been discussed in the field of science and technology in the past such as second, third and fourth harmonic generators for Nd: YAG, Nd: YLF lasers and for electro-optical applications such as Q-Switches for Ti: Sapphire, Alexandrite lasers, as well as for acousto-optical applications (Muncheryan, 1991; Shen, 1984; Sakai, 1982; Ramasamy *et al*, 1999; Santhana Raghavan *et al*, 2002). Delonix elata (Vathanarayana – tamil name) belongs to the family of fabaceae. Plant extract contains chemical constituents like alkaloids, tannins, triterpenoids, steroids, flavonoids and glycosides [Bharathi *et al*, 2014; Kumar *et al*, 2013; Wijayasiriwardena *et al*, 2009). Literature reports on medicinal uses of Delonix elata leaf extract revealed the pharmacological actions similar to anti- inflammatory activity (Phani Kumar *et al*, 2014; Sini *et al*, 2010) antioxidant activity, anti-cancer regimens (Manimekalai *et al*, 2011; Doss *et al*, 2009) and which kill or stop the growth of microorganisms including both bacteria and fungi(Madhu *et al*,2009). From this motivation ADP and Delonix elata leaves extract were used as additive agent to prepare crystal by slow evaporation techniques. The grown pure ADP and Delonix elata leaves extract doped ADP crystal have been analyzed by various characterization subjected to Fourier Transform Infrared Spectroscopy (FT-IR),

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UV-Vis Spectroscopy, X-ray Diffraction (Powder XRD, Single XRD) Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDAX), Vicker's Micro hardness and the Thermo gravimetric analysis (TGA) and Differential thermal analysis (DTA) .

Experimental Procedure

Ammonium dihydrogen phosphate (ADP) is a well known inorganic salt, which has been purified by continual recrystallization using the method of dissolving in distilled water. Then the solution of ADP salts have been prepared in saturation condition by stirring well for five hours frequently using magnetic stirrer, turn over the salts have been dissolved in water. After that the prepared solution has been transferred into two clean Petri dishes and kept for crystallization at room temperature in a settle down place.

Table 1 Vibrational Band Assignments of Pure and Delonix elata leaf extract doped ADP Crystals

Wave number (cm^{-1})		
Pure ADP	**Delonix elata leaves extract doped ADP**	**Functional group assignments**
3139	3127	O-H Stretching Vibration
2353	2410	N-H Stretching of Ammonia
-	1736	Asymmetric B-O Stretching
1640	1641	Binding vibration mode of O-H group
1412	1442	Bond vibration of Ammonia
1287	1291	Combination band of P-O Stretching Vibration
1097	1116	P-O stretching
911	919	P-O-H stretching Vibrations
558	551	PO_4Vibrations
452	459,440,415	PO_4 Vibrations

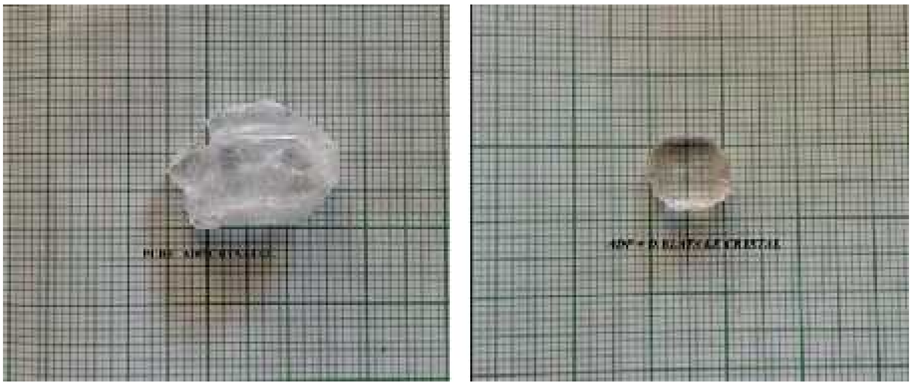

Fig 1 Photographs of the Pure ADP and Delonix elata leaf extract doped ADP Crystals

After three days the nucleation takes place and a seed crystal in Petri dish has been obtained. A supersaturated solution of pure ADP and 10ml of Delonix elata leaves extract doped ADP at room temperature has been prepared by same processes and then filtered into two clean Petri dishes. The good quality seed has been suspended in respective Petri dishes. A slow evaporation method has been employed to grow ADP and Delonix elata leaves extract doped crystal. After completion of growth run, the crystals have been harvested and subjected to various characterizations.

RESULTS AND DISCUSSION

Fourier Transform infrared spectroscopy (FT-IR)

The FT-IR analysis provides information about the chemical bonding or molecular structure of materials. The FT-IR investigations were also carried out on the powdered samples of pure ADP and D.elata leaf extract doped ADP crystals. The spectrum was observed from Perkin Elmer spectrum RXI spectrometer in the region 4000 to 400 cm^{-1} using KBr pellet. The prominent peaks in the FT-IR pattern have been indexed as shown in Fig 2. Many useful observations were observed and to identify the different functional groups of pure and doped ADP crystal. The absorption peaks corresponding to the both pure and doped ADP crystal the molecular group of vibrations are tabulated in table1.

For pure ADP crystal, the band 3139 cm^{-1} was assigned to stretching vibration of O-H group. The band 1287 cm^{-1} due to combinations bands of stretching (Rajesh *et al*, 2009). The N-H bonding of NH_4 stretching vibration assigned at 1640, 1412 cm^{-1} (Ananthi *et al*, 2011). The vibrational stretching mode of P-OH group was observed at 1097 and 911 cm^{-1}. The vibrational modes of PO_4groups were observed at 558 and 452 cm^{-1}.

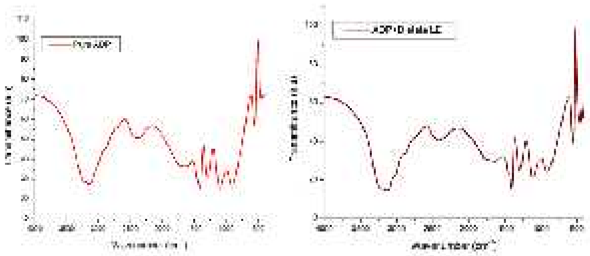

Fig 2 FT-IR spectrum of Pure ADP and Delonix elata leaf extract doped ADP Crystals

In order to Delonix elata leaves extract doped ADP crystal spectrum is almost the same as pure ADP except that a few shifting of peaks is noticed. The band 3156 and 3127 represent the O-H stretching of water groups and the band 2410, 1291 cm^{-1} was assigned at combination band of N-H Stretching of Ammonia. The bands of 1641 cm^{-1} was assigned to vibrational mode of OH group. The vibrational mode of P-OH was observed at band 1116 and 919 cm^{-1} (Anitha Hudson *et al*, 2014). The vibrational bands of 551, 459 cm^{-1}were observed at the stretching vibration modes of PO_4 groups. Also some new bands are obtained in the doped crystal identically the band

1736 cm^{-1} represents the asymmetric B-O Stretching and P=O deformation at 440, 415 cm^{-1} has appeared in the FT-IR spectrum of doped ADP.

Single and Powder X-ray diffraction analysis (XRD)

The cell parameters have been determined by single crystal XRD analysis for leaf extract doped ADP grown crystals done using Bruker Kappa APEX II single crystal X-ray diffractometer. The calculated lattice parameter values are a= 7.53 Å, b= 7.53 Å, and c= 7.58 Å with angles α= β= γ= 90̊ .The grown Delonix elata leaves extract doped ADP crystal belongs to tetragonal system with I42d space group. The Lattice parameter values of Delonix elata leaves extract doped ADP single crystals are scheduled in table 2.

Table 2 Unit cell parameters of pure ADP and Delonix elata leaf extract doped ADP crystals.

Crystal	a(Å)	b(Å)	C(Å)	Volume(A^3)	α=β=γ	System
Delonix elata leaves extract doped ADP	7.53	7.53	7.58	430	90̊	Tetragonal

The formation and quality of pure and Delonix elata leaf extract doped ADP crystal compounds were checked by powder XRD analysis using a XPERT-PRO diffractometer with operating voltage 40 kV at a current strength of 30mA. The samples were subjected to Cu Ka radiation and the scanning was done in the region of 10-80°. The images obtained were compared with Joint Committee on Powder Diffraction Standard (JCPDS) library to account for the crystalline structure. Fig 3 shows the XRD pattern of pure and doped crystal.

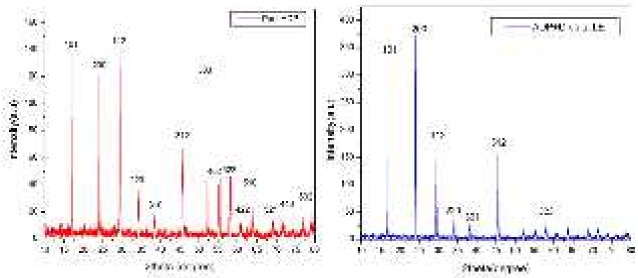

Fig 3 XRD spectrum of Pure ADP and Delonix elata leaf extract doped ADP Crystals

From the figure there are some changes in peak intensities and slight shifts in peak positions. These values are close to the corresponding JCPDS values of 01-076-0415 and 01-087-2351 for pure ADP with very hypothetical changes due to doping. The size of the crystalline are calculated using the Scherrer's equation such as 25.2 nm and 24 nm via pure and doped crystal. The crystallite sizes depend on the nature of the dopant. The changes in peak intensities, peak shifts in the XRD and too little increase in lattice parameters could be recognized to the strain developed by the incorporation of dopants.

SEM and EDAX analyses

The scanning electron microscope (SEM) investigation of the pure and D.elata leaf extract doped ADP crystal were monitoring in Fig 4(a)&(b) the analysis recording JEOL JSM 6390 electron microscope.

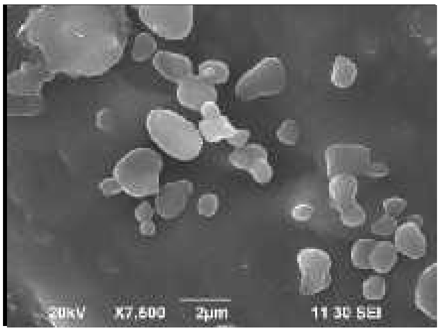

Fig 4(a) SEM image of Pure ADP crystal

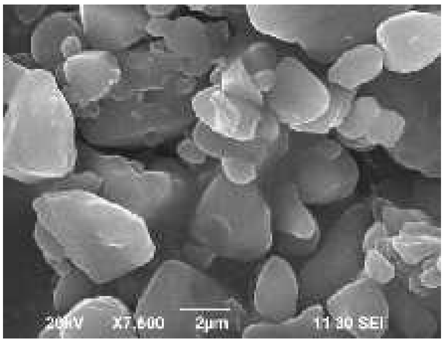

Fig 4(b) SEM image of D.elata leaf extract doped ADP crystal

For pure and doped the surface of the crystal are roughly spherical and course shape. The surface change of dopant SEM structure reveals the presence of dopant. Fig 5 shows the Energy Dispersive X-ray spectrum analysis of Pure and doped crystals. From EDAX spectrum the chemical composition weight has been calculated. The estimation percentages of O, P and Zr in pure ADP and D.elata leaf extract doped ADP crystals are reported in table 3.

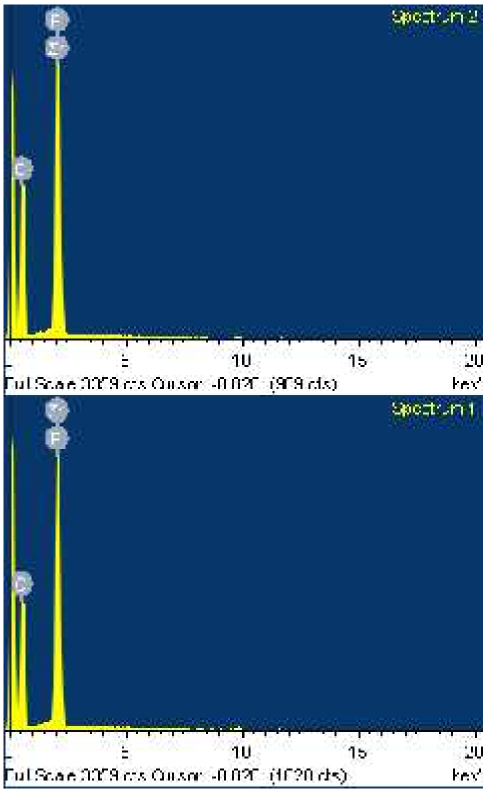

Fig 5 EDAX spectrum of Pure ADP and Delonix elata leaf extract doped ADP Crystals

Table 3 Estimated Weight Percentage of Pure ADP Crystal

Element	Weight %	Atom %
O	58.12	81.27
P	17.72	12.80
Zr	24.17	5.93
Total	100.00	100.00

Table 4 Estimated Weight Percentage of D.elata Leaf Extract Doped ADP Crystal

Element	Weight %	Atom %
O	58.21	81.72
P	16.68	12.09
Zr	25.12	6.19
Total	100.00	100.00

Vicker's Micro hardness

Micro hardness tests are useful to find the mechanical hardness of the crystal grown. The mechanical property of the grown pure and Delonix elata leaf extract doped ADP crystal has been determined by Vicker's Micro hardness test with a diamond indenter at various loads from 25g to 100g.

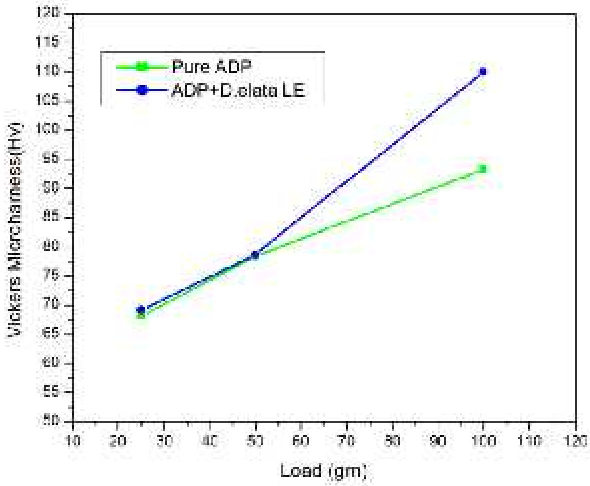

Fig 6 Micro hardness vs Load graph for Pure and Delonix elata doped ADP crystals

The hardness values were calculated using the formula:

$$Hv = 1.8544(P/D^2)\ kg\ mm^2$$

Where Hv is the Vickers hardness number, P is the indenter load in g and D is the diagonal length of the impression in millimeter (mm). The microhardness value was taken as the average of the several impressions made with both diagonals being measured. A plot had drawn between Load Vs Hardness number for ADP and doped ADP crystals shown in Fig 6. It is observed that the hardness of the pure ADP is less significant than that of the doped ADP crystals. At 100g the hardness number of ADP and doped ADP crystals is 93.3Hv and 110Hv respectively. This result shows the dopent is perfectly located in the ADP crystal lattice and increases the mechanical property.

UV-Vis spectral studies

The UV-Vis spectrum of the crystal was recorded in the region 200-700 nm using SIGMANDU spectrometer. It is seen that the doped ADP crystal has better lower cut off wavelength than that of pure ADP crystal. Pure ADP crystals have more absorbance in the entire spectral range in an evaluation with the doped specimen as shown in Fig 7. The spectrum indicates that the pure and doped ADP crystals have minimum absorption in the entire region between 200 - 800 nm. It is interesting to note that the leaf extract doped ADP crystal has reduced absorption when compared to pure ADP. If the UV-Vis spectrum of a crystal shows minimum absorption and lower cut off wavelength then the probability that the crystal possessing NLO active is more (Delci *et al*, 2012). It is observed that in leaf extract doped ADP the above stated form is satisfied hence it can be done that the crystal is NLO active. Absorption in the ultraviolet region arises from electronic transitions associated within the sample. The band gap energies were established using the formula **Eg = hc/λ**, where h is the Planck's constant and c is the velocity of light. It was seen that the band gap energy is 4.5 eV for pure ADP and 4.9 eV for doped ADP. Therefore the improved band gap energy of 4.9 eV and better crystal transparency in doped ADP can be attributed to the presence of leaf extract.

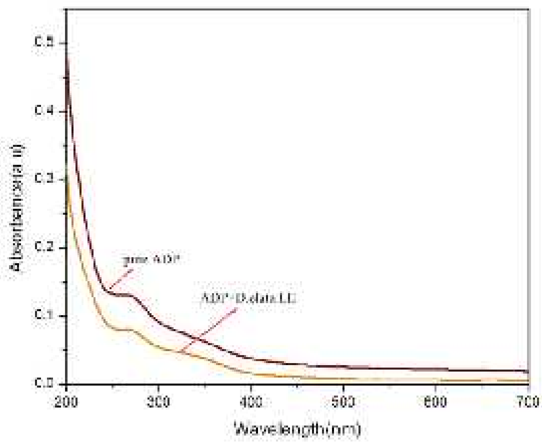

Fig 7 UV-Vis spectra observed for the Pure and D.elata doped crystal

Thermal stability (TG/DTA)

Thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) curves were obtained for the grown Pure and Delonix elata doped ADP crystals using a thermal analyzer NETZSCH STA 449F3 in the nitrogen atmosphere in the temperature range of room temperature to 900 °C at a heating rate of 10 °C/min. Thermal stability the TGA and DTA curves for pure ADP and D.elata leaf extract doped ADP crystals are shown in Fig 8 (a) & (b)

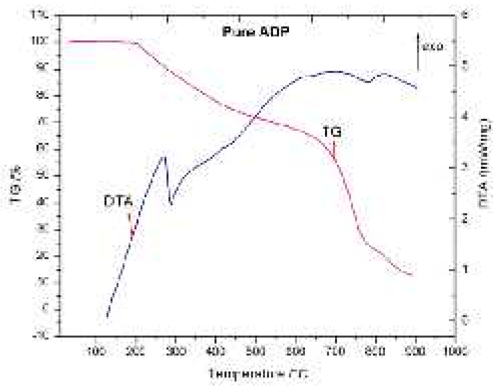

Fig 8(a) TG/DTA Curve for Pure ADP

It can be understood that pure ADP and doped ADP are thermally stable there is no weight loss up to 197.5 °C and 201

°C respectively. The decomposition takes place at these temperatures. This indicates that there is no inclusion of water in the crystal lattice, which was used as the solvent for crystallization (Rajesh *et al*, 2010). The difference in thermal stability observed between these two crystals makes us to understand that doped ADP molecules have entered into the Pure ADP crystal matrix in the case of doped crystals. However, above this temperature, weight loss has been observed.In the DTA, the strong endothermic peak located at 287 °C and 284 °C depict the crystallization of some of the phases of the decomposed materialshow the good crystallinity of the specimens.

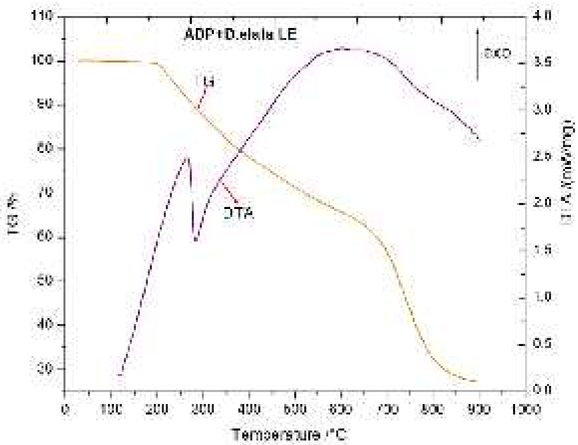

Fig 8(b) TG/DTA Curve for Delonix elata leaf extract doped ADP

CONCLUSION

Transparent, colourless crystals of pure and Delonix elata leaf extract doped ADP crystals were grown by slow evaporation technique at room temperature.From the UV-vis absorption spectra reveals that grown crystals having lower cut-off wavelength is found better optical transparency and for good NLO efficiency. FT-IR study confirms the presence of functional groups in crystals. SEM and EDAX analysis confirm the morphology and chemical composition of the grown crystals. Finally a close observation of XRD profiles both sample belongs to tetragonal system with I42d space.

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