



PHYSICS

GROWTH AND CHARACTERIZATION OF DOPED ADP CRYSTAL

T. Ananthi¹, S. Mary Delphine^{1*}, M. Mary Freeda¹, R. Krishna Priya², Abdul Wahab Almusallam³

¹Department of Physics, Holy Cross College, Nagercoil -4

²Department of Physics, Rajas International Institute of Technology for Women, Nagercoil-1

³Department of Chemical Engineering, Kuwait University, Kuwait

Abstract

Pure and impurity added (urea) Ammonium dihydrogen orthophosphate (ADP) single crystals were grown by the slow evaporation technique. Crystallinity of the pure and doped crystal has been studied by XRD analysis. Fourier transform infrared (FTIR) studies confirm the functional group of the crystals. Thermal studies (TG/DTA) confirm that decomposition temperatures of the doped crystals have been decreased.

Keywords: ADP crystals, X-ray diffraction, Microhardness, Thermal studies

Introduction

Ammonium dihydrogen orthophosphate (ADP) $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ is an interesting material [1-4], and it belongs to isomorphous series of phosphates and arsenates that presents a strong piezoelectric activity. ADP is antiferroelectric below 148.5 K and belongs to $P2_1 2_1 2_1$ space symmetry group, while above this temperature it becomes paraelectric having $I 4/2 d$ symmetry [5-7]. ADP belongs to scalenohedral class of tetragonal crystal systems. ADP has unit cell parameters of $a = b = 7.510 \text{ \AA}$ and $c = 7.564 \text{ \AA}$ [8,9]. It is known that, very little amount of additives can strongly suppress the metal ion impurities and promote the crystal quality [10,11]. Oxalic acid and amino acids as additives in ADP crystals give appreciable change in optical, thermal, dielectric and mechanical behaviors [12,13]. In a crystal metastable zone width is an essential parameter for the growth of good crystals from solution. Organic additives urea and thiourea increase the metastable zone width. In ADP crystal, using urea as additive, metastable zone width increased by 3.7°C , saturated at 30°C [14]. The effect of additives depends on the additive concentration, super saturation, temperature and PH. The growth promoting effect is observed in the presence of organic additives [14, 15, 16, 17,]. Generally, anion and cation impurities in the solution are adsorbed in to (101) of (1 0 0) point faces of ADP crystal. This selectivity on ions adsorption has been attributed to the orientations of anion $(\text{H}_2\text{PO}_4)^-$ and cation $(\text{NH}_4)^+$ as the respective crystal faces [18,19]. P. Rajesh et al, have discussed the effect of oxalic acid as additive in ADP in different molar ratios and studied the crystal properties. They also have studied the effect of an organic additive, Thiourea, in ADP at different molar ratios [8,13].

For higher concentration of impurities, the lattice distortion is less. The strongest argument is that if

higher amount of impurities are adsorbed at the surface terrace, it might possibly retard the rest of the impurities from entering into the lattice or might entirely block the impurities [20]. The measurement of dielectric constant and dielectric loss as a function of frequency and temperature is of interest both from theoretical point of view and from the applied aspects [21]. Dielectric constant is one of the basic electrical properties of the solids. Dielectric properties are correlated with the electro optic properties of the crystal [22].

ADP is widely used in second, third and fourth harmonic generator for Neodymium-doped Yttrium Aluminum garnet ($\text{Y}_3\text{Al}_5\text{O}_{12}$) Nd:YAG laser and Neodymium-doped Yttrium Lithium Fluoride (YLiF_4) Nd:YLF laser, frequency conversion, Q switch and quantum electronics as well as electro-optical and acousto-optical applications [23-28]. Particularly, optical crystals with lower impurity and higher damage threshold are required for inertial confinement fusion [27,29]. The behavior of these crystals in the radiation fields includes formation of the optical waveguide in these crystals [30,31]. Many devices such as Electro-Optic (EO) modulators and second harmonic generators are developed using these crystals [32]. They have attracted the interest of many theoretical and experimental researchers, probably because of their simple structure and very fascinating properties.

A most conspicuous feature in the development of physics of these crystals is the close interplay between theory and experiments, which makes significant progress in understanding their microscopic properties [33]. Additives made an effect on growth, habit modification and structure of ADP [34-36]. An impurity can suppress, enhance or stop the growth of a crystal completely [37,38]. ADP crystals grown from deuterium gives more than 80% of transparency in the entire

* Corresponding Author, Email: delphine_mry@yahoo.co.in

visible region[39]. In the conventional crystal growth techniques, ADP crystal gives only 52% of transparency [40]. It is a known fact that urea is a simple organic nonlinear optical material and has no common ion with ADP. Hence, if urea is added as impurity into the lattice of ADP, either replacement of NH_4^+ or $(\text{H}_2\text{PO}_4)^-$ ion is not possible [41]. Crystals with high conversion efficiencies for second harmonic generation are desirable in various fields.

To improve growth and optical characteristics of ADP crystals, urea is added in different molar concentrations useful for academic and industrial purposes. Considering the above discussion in our mind, we have grown ADP single crystal with urea as impurity in very small molar ratios (0.005, 0.010, 0.015, 0.020, 0.025 & 0.030) and studied optical, structural, thermal, mechanical and dielectric properties by slow evaporation solution growth. The results were compared with some earlier reported values.

Experimental Details

Analytical reagent grade (AR) samples of $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ and urea along with deionized water were used for the growth of single crystals by slow evaporation method. ADP was added with urea in different ADP:impurity molar ratios, viz. 1:0.000 (pure ADP), 1:0.005, 1:0.010, 1:0.015, 1:0.020, 1:0.025 and 1:0.030 respectively.

350 ml supersaturated solution of ADP was prepared at room temperature. Pure ADP crystals were obtained by transferring 50 ml of the supersaturated solution of ADP in a beaker, which was kept closed with a porously sealed cover. ADP doped with urea can be obtained by pouring 50 ml ADP supersaturated solution with urea prepared by the same procedure. Nucleation occurs within 3 days and crystals reach a large size in 14 days for all crystals. Grown crystals are very stable, colorless and exhibit tetrahedral morphology. Relatively large crystals up to $2 \times 1 \times 0.5 \text{ cm}^3$ were obtained in ADP doped solution.

Results and Discussions

Structural analysis

The crystal structure was investigated by powder X-ray diffraction, which was performed on a D8 advance (Bruker-axs, Germany) automatic X-ray diffractometer using nickel-filtered $\text{Cu K}\alpha$ irradiation. The ground fine powder was scanned in steps of $0.001^\circ/\text{min}$ over a 2θ range of $10 - 80^\circ$. The lattice parameters were calculated by computer program - TOPAS. XRD values of ADP crystallites are in good agreement with standard JCPDS card No. 850815. There are no other phases that were observed beside the tetragonal system. Figs 1 (a), (b), (c), (d), (e), (f) and (g) show the XRD patterns of pure and urea doped (0.005, 0.010, 0.015, 0.020, 0.025 and 0.030) ADP

crystals in all molar concentrations. The preferred orientation peaks of pure and urea doped ADP crystals are (2 0 0), (1 1 2), (1 0 1), (1 1 2) and (2 0 0). Comparison of lattice with the JCPDS values has been presented in Table 1, which agrees well with the previous conclusions [12, 42-44]. The addition of urea in ADP has less effect on lattice parameters. This shows that large amount of impurity molecules could not enter into lattice sites of ADP. This similar result was reported for ADP crystal doped with thiourea [20]. The change in lattice parameters 'a' and 'b' suggest that the structure of urea doped crystals are slightly distorted when compared to pure ADP crystal.[9]. The value of lattice parameters of urea doped ADP crystals are found to be varied with the addition of urea concentration in solution. The value of 'c' is found inconsistent and this finding may be related to the irregular growth and essentially due to the non uniform absorption of the impurities on the growing face[20]. From the XRD spectrum of pure and urea doped crystals, it is seen that there is no additional peaks, but only change in the intensity of the peaks. This shows the absence of any additional phase due to doping [12].

Fig. 1(a)

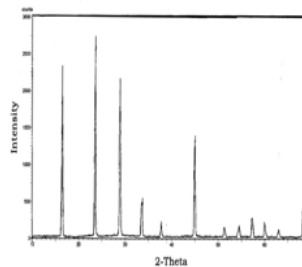


Fig. 1(b)

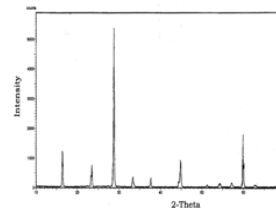
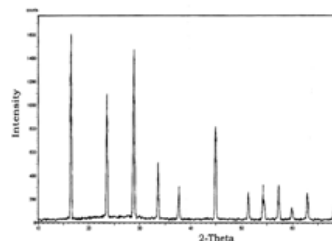


Fig. 1(c)



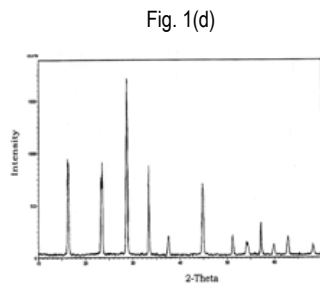


Fig. 1(d)

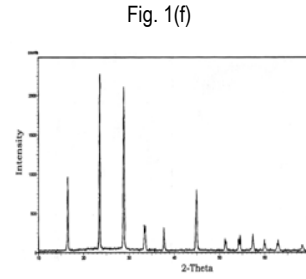


Fig. 1(f)

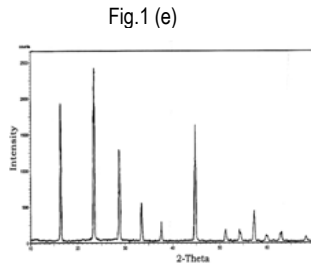


Fig.1 (e)

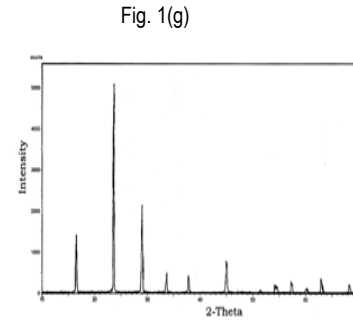


Fig. 1(g)

Table 1 - Comparison of Lattice Constant with the JCPDS values and Early reported values

System	a (Å)	b (Å)	C (Å)
JCPDS	7.499	7.499	7.549
Early reported [27,28]	7.502	7.502	7.546
Early reported [29,30]	7.510	7.510	7.564
1 : 0.000 (pure ADP)	7.5274	7.5274	7.5415
1 : 0.005 (ADP:urea)	7.5429	7.5429	7.6082
1 : 0.010 (ADP:urea)	7.5421	7.5421	7.5820
1 : 0.015 (ADP:urea)	7.5814	7.5814	7.5027
1 : 0.020 (ADP:urea)	7.5431	7.5431	7.6092
1 : 0.025 (ADP:urea)	7.5621	7.5621	7.5929
1 : 0.030 (ADP:urea)	7.5744	7.5744	7.6127

FTIR Spectroscopy

FTIR spectra of doped crystal were recorded using a JASCO FTIR 410 spectrometer in the range 400-4000 cm^{-1} by KBr pellet technique. The influence of additives produces shift in the vibration frequencies of functional groups and the percentage of

transmission. FTIR spectra of pure and urea doped(0.005,0.010,0.015,0.020,0.025 and 0.030) ADP crystals are shown in figs 2(a),(b),(c),(d),(e),(f) and (g). Strong band centered at about 3260 cm^{-1} is due to OH stretching and water bending. The infrared bands observed around 2364 cm^{-1} is due to the combination

band of vibrations occurring at 1293 and 1290 cm^{-1} respectively. The peak at 1287 cm^{-1} is due to one of the vibration of combination band. The infrared band at 1652 cm^{-1} is due to water bending vibrations and the peak at 1409 cm^{-1} is due to the bending vibrations of ammonium. The band at 1092 cm^{-1} is due to O-H vibrations. The peaks observed around 919 and 552 cm^{-1} produces a shift in the peak positions of P-O-H and PO_4 vibrations respectively.

Table 2 shows the assignment of same selected FTIR bands (cm^{-1}) of pure and urea doped ADP crystals. For comparison early reported FTIR data [44] is given in the table.

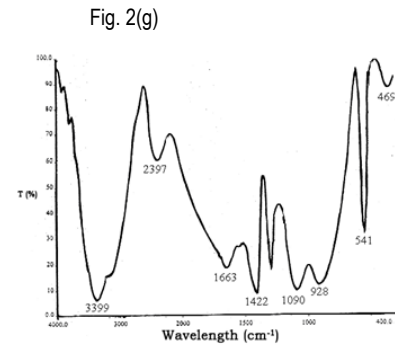
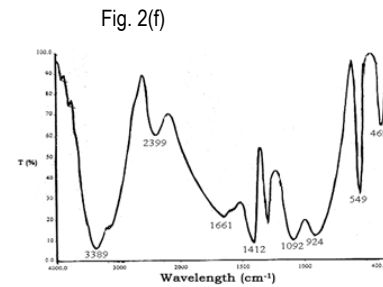
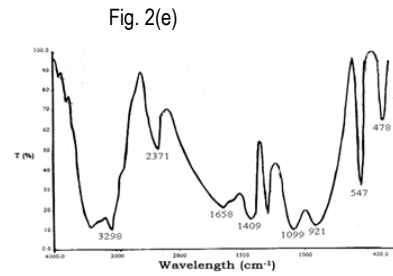
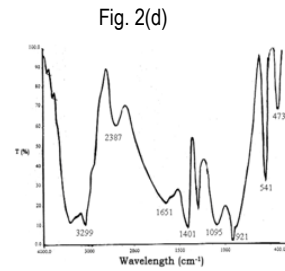
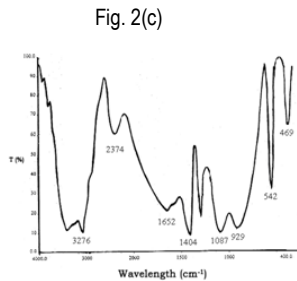
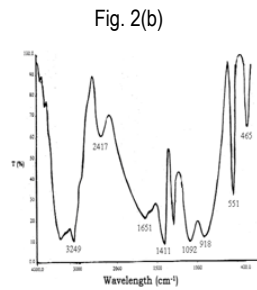
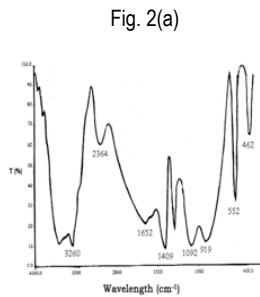


Table 2 - Assignment of some selected FTIR bands (cm⁻¹) of pure and urea doped crystal

Early reported [44]	ADP:Urea							Band Assignments
	1 : 0.000	1 : 0.005	1 : 0.010	1 : 0.015	1 : 0.020	1 : 0.025	1 : 0.030	
3700-2700	3260	3249	3276	3299	3300	3289	3289	O-H stretching and water bending
2370	2364	2417	2374	2387	2371	2399	2397	Combination band of vibrations occurring at 1293 cm ⁻¹ and 1290 cm ⁻¹
1646	1652	1651	1652	1651	1658	1661	1663	Bending vibrations of water
1402	1409	1411	1404	1401	1409	1412	1422	Bending vibrations of NH ₂
1090 & 930	1092 & 919	1092 & 918	1087 & 929	1095 & 921	1099 & 921	1092 & 924	1090 & 928	P-O-H vibrations
544 & 470	552 & 462	551 & 465	542 & 469	541 & 473	547 & 478	549 & 469	541 & 469	PO ₄ vibrations

Thermal analysis

Thermal analysis was performed using Perkin-Elmer diamond TG/DTA instrument in nitrogen atmosphere at a heating rate of 5°C/min. Figs 3(a),(b),(c),(d),(e),(f) and (g) show the TGA and DTA spectra of pure and urea (0.005, 0.010, 0.015, 0.020, 0.025, 0.030) doped ADP crystals. The thermal properties of a crystal are important in crystal growth and its application. Thermal expansion, specific heat and thermal conductivity are the basic properties for lasers and high power systems. When a laser beam interacts with a Non Linear Optical (NLO) crystal, certain amount of the incident energy is converted to thermal energy, thus leading to a temperature gradient inside the crystal. For a crystal with large specific heat, the change in thermal gradient of the crystal is small. These crystals might have large damage threshold and can potentially be used in high power laser systems [45].

Fig. 3(a)

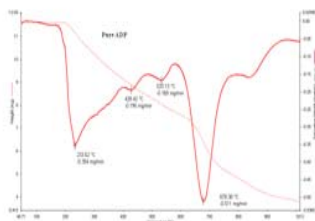


Fig. 3(b)

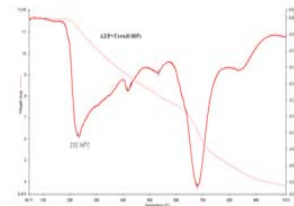


Fig. 3(c)

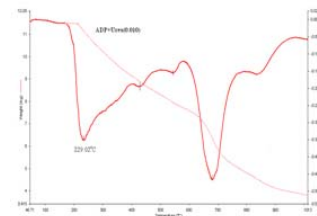


Fig. 3(d)

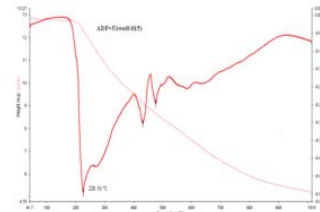


Fig. 3(e)

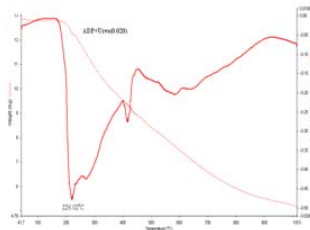


Fig. 3(f)

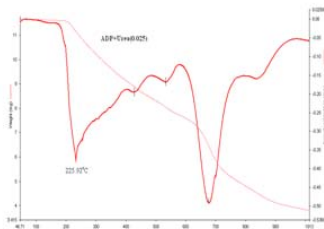
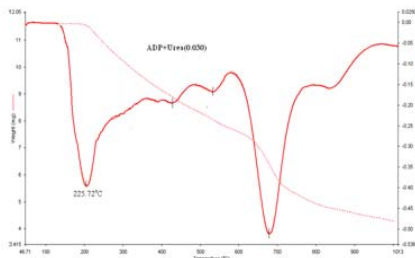


Fig. 3(g)



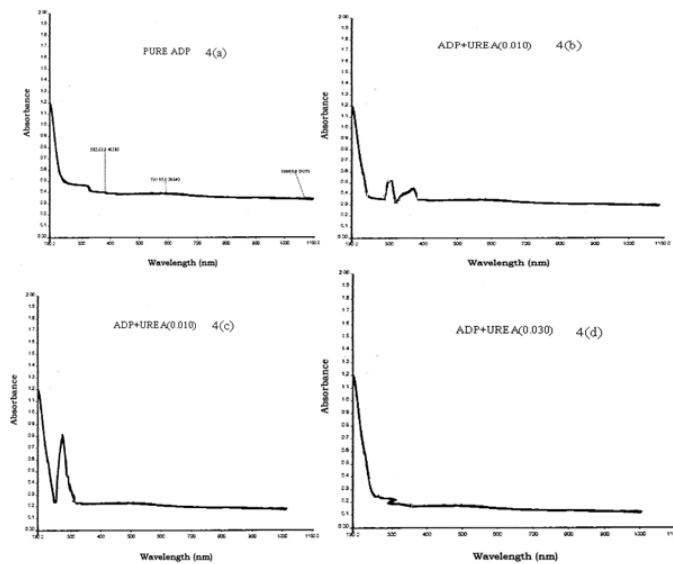
The TG/DTA curves for pure and urea doped ADP crystals showed that the first decomposition starts

between 215.86°C to 210.16°C for pure and doped ADP crystals. The weight loss of the crystals might be devoid of any physically entrapped water or water of crystallization[46], which confirms the absence of water molecules in the grown crystals. The weight loss in these temperatures are consistent with the decomposition temperature of the compounds. The DTA curve of pure ADP has a major endothermic peak at 233.62°C and

urea doped ADP at 232.06°C, 229.02°C, 226.10°C, 226.02°C, 225.92°C and 225.72°C respectively. The melting point of urea is 135°C [science lab-material safety data sheet]. The addition of urea decreases the decomposition temperature by 7°C for doped(0.030) crystal. This shows that the urea molecules present inside the crystal could have weakened the lattice partially. For other impurities nickel sulphate and L-asparagine monohydrate the decomposition of ADP increased by 8°C and 10°C respectively[47,48]. This appears to be in order as the urea present inside the crystal could have partially out diffused thus partially damaging the lattice. Same results were observed, when the measurement was repeated several times.

UV-Visible

The large transmission in the entire visible region enables ADP to be a good material for electro – optic and NLO applications [13,49]. The reported value of the optical transparency for ADP is from 184 to 1500 nm [50]. The spectra were recorded in the wavelength region from 190 to 1100 nm using Lambda 35 spectrophotometer. Crystals with a thickness of 2 mm were cut and polished at face (001) without any coating is used for the optical measurements. UV-Vis spectra recorded for pure and urea doped ADP crystal are shown in fig. 4(a), (b), (c), and (d).

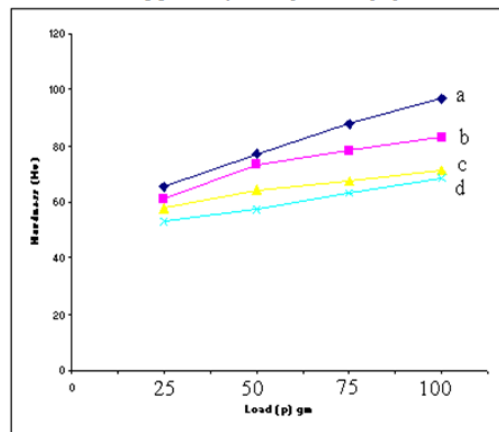


In the present study, the results are in good agreement with the reported values [51,52]. There are steps in the transmission curves of pure and doped ADP crystals in the low wavelength region. This is due to change of optics in the photometer [52]. It was observed that the pure ADP has 62% transmission, whereas urea doped (0.005, 0.010 and 0.015) ADP has enhanced transmittance value than pure ADP. It is found that the cutoff wavelength is nearly equal [53] for all crystals. The optical transparency of the ADP crystal is increased by the addition of impurities. The addition of urea dopants with optimum conditions to the solution is found to suppress the inclusions and improve the quality of the crystal with improved transparency [52].

Microhardness

Suitably cut and polished samples (with known dimensions) are subjected to dielectric studies using HIOKI 3532-50 HITESTER LCR meter, with a conventional four terminal sample holder for investigations involving temperature variations and a conventional two terminal sample holder (westphal) for only ambient conditions. Fig 5 shows the relation between the hardness and load of urea doped ADP crystals. Hardness is the resistance offered by a solid to the movement of dislocation. Practically, hardness is the resistance offered by a material to localized plastic deformation caused by scratching or by indentation. Due to the application of mechanical stress by the indenter, dislocations are generated locally at the region of the indentation. Higher hardness value of a crystal indicates that greater stress is required to form dislocation thus confirming greater crystalline perfection [47].

Fig. 5: Micro hardness Vs Load (a)Pure ADP(b)ADP:Urea(0.010) (b)ADP:Urea(0.020) (b)ADP:Urea(0.030)



The micro – indentation test is a useful method for studying the nature of plastic flow and its influence on the deformation of the material. Also, the hardness of the crystal is dependent on the type of chemical bonding, which may differ along the crystallographic direction [54]. Hardness is one of the important deciding factors in selecting the processing (cutting, grinding and polishing) steps of bulk crystal in fabrication of devices based on the crystals. It is therefore important to study the mechanical properties of NLO crystals[55]. The hardness of the crystal is

calculated using the relation $H_v = 1.8544 \frac{P}{d^2}$, where

H_v is the vicker's hardness number, P is the indentation load in Kg and d , the diagonal length of the impressions in nm. The micro hardness value was taken as the average of the several impressions made.

The hardness results show that the hardness increases with increase in load for pure and urea doped ADP crystals. At 200gm load cracks have been observed for all crystals. The addition of urea decreases the hardness of the crystal. Similar results were also observed in ADP crystals [40]. Microhardness value of the pure ADP crystal decreases with the increase of urea concentration in the solution. In the case of thiourea and amino acid impurities in ADP crystal, similar results were reported (8, 12). The H_v vs load for pure and doped ADP crystals are tabulated in Table 5.

Table 5. Hv vs load for pure and doped ADP crystals

Sample	Load			
	25 gm	50 gm	75 gm	100 gm
ADP	65.6	77.4	87.6	96.8
ADP+0.010	61	73.6	78.2	83.1
ADP+0.020	58	64.4	67.5	71.2
ADP+0.030	53.1	57.1	63.1	68.5

Dielectric studies

The dielectric constant and dielectric loss were measured using Agilent 4284-A LCR meter. Crystals of 3mm thickness and 9mm diameter were cut from various parts of the crystals grown by solution and more polished using solvent polishing technique. The dimensions of the samples were determined using digital electronic vernier calliper (LC = 0.001 cm). Two opposite surfaces across the breadth of the crystal were made with good quality of silver paste to get good ohmic contact. Using the LCR meter, the capacitance of these crystals was measured in the frequency range of 50 Hz to 5 MHz at various temperatures (30°C, 40°C and 60°C). The dielectric constant of the crystals was calculated using the relation .

$$\epsilon_r = C_{cry} / C_{air}$$

Where C_{cry} is the capacitance of the crystal and C_{air} is the capacitance of same dimension of air.

Fig. 6

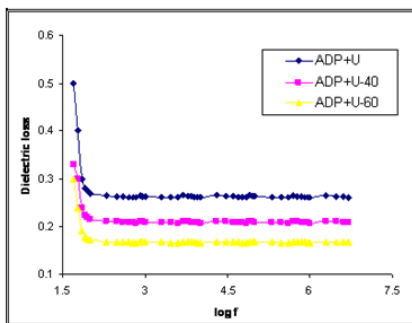
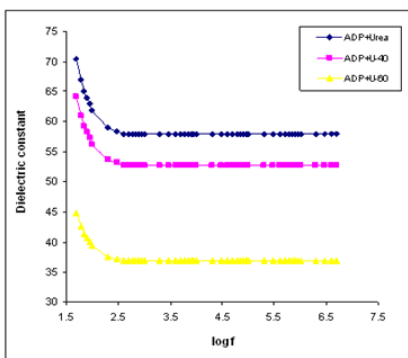


Fig. 7



Conclusion

Organic compound (urea) was successfully doped with ADP crystal and found that these additives can affect the nucleation of ADP from aqueous solutions. Lattice parameters were calculated from the XRD characterization. The FTIR spectrum shows that organic additives(urea) were entered into the ADP crystals. The decomposition temperature of these crystals has been studied by Thermal Analysis. Optical studies confirm higher transmittance for pure ADP crystal than urea added ADP crystal.

Acknowledgement

The Authors acknowledge Dr.Abdul Wahab Almusallam, Department of Chemical Engineering, Kuwait University, Kuwait for his valuable discussions and suggestions to carryout this paper.

References

1. Davey R J and Mullin J W 1976 Krist. Technol. 11 22.
2. Levina I M and Belyustin A V 1980 Soviet Phys. Cryst. 25 209.
3. Nagalingam S, Vasudevan S and Ramasamy P 1981 Cryst. Res. Technol. 16 647.
4. Ramesh R and Mahadevan C 1998 Bull. Mater. Sci. 21 287.
5. M.E. Lines, A.M. Glass, Principles and Applications of Ferroelectrics and Related Materials, Clarendon Press, Oxford, 1977.
6. N.G. Parsonage, L.A.K. Staveley, Disorder in Crystals, Clarendon Press, 1978.
7. L.Tenzer, B.C. Frazer, R. Pepinsky, Acta Cryst. 11 (1958) 505.
8. N. P. Rajesh, et al, Mater. chem. Phy 76 (2002) 181-186]
9. R.W.G. Wyckoff, crystal structure, 2nd edition, Interscience, New York, 1960, P.160
10. Abdul-kadar, J. Mater. science-mater . Electron, 2(1991)7.
11. J.Podder, J.Crystal.\growth 237(2002)70.

12. P.V. Dhanaraj, G. Bhagavannarayana and N.P. Rajesh, *Materials Chemistry and Physics*, 112 (2008) 490-495.
13. P.Rajesh, et al, *J.Cryst.Growth* 311(2009)1611.
14. N.P. Rajesh, et al, *cryst- Res. Technol.* 36 (2001) 55-63.
15. G. Bhagavannarayana, S. Parthiban, S.P. Meenakshisundaram, *J. Appl. Crystallogr.* 39 (2006) 784.
16. V.A. Kuznetsov, T.M. Okhrimenko, M. Rak, *SPIE Proc.* 3178 (1997) 100.
17. G. Li, L. Xue, G. Su, Z. Li, X. Zhuang, H. Ha, *Cryst. Res. Technol.* 40 (2005) 867.
18. D. Xu, et al, *J. mol. Struct.* 740 (2005) 37
19. X. Xu, et al, *Opt. mater.* 23 (2003) 409
20. A.Jayarama ,S.M.Dharmaprakash, *Applied surface science*,253(2006) 944-949.
21. S. Goma, et al, *mater. Lett.* 60 (2006) 3701.
22. H.M. Lin, et al, *J. Appl. Crystallogra* 22(1989)209.
23. L. Glasser, *Chem. Rev.* 75 (1975) 21.
24. M.J. Gunning, R.E. Raab, W. Kucharczyk, *J. Opt. Soc. Am. B* 18 (2001) 1092.
25. N. Zaitseva, L. Carman, *Prog. Cryst. Growth ch.* 43 (2001) 1-118.
26. S.A.de Vries, et al, *J. Cryst. Growth* 205 (1999) 202-214.
27. Yokotani, T. Sasaki, K. Yamanaka, C. Yamanaka, *Appl. Phys. Lett.* 48 (1986).
28. S. Sen Gupta, T. Kar, S.P. Sen Gupta, *Mater. Chem. Phys.* 58 (1999) 227.
29. Yusuke Asakuma, et al, *Appl. Surf. Sci.* 254 (2008) 4524.
30. Green M L H, Marder S R, Thompson ME et al., *Nature*, 330 (1987) 360.
31. Marder S R, Tiemann B G, Perry J W et al., *Materials for Non-linear Optics Chemical Perspectives* (American Chemical Society, Washington), 1991, p. 280.
32. Dongfeng Xue and Henry Ratajczak, *Journal of Molecular Structure: THEOCHEM* 716 (2005) 207-210.
33. R. Ananda Kumari, *Indian Journal of Pure & Applied Physics*, Vol.47, May2009, pp. 369-371.
34. R. J. Davey, J.W. Mullin, *J. Cryst. Growth* 26 (1974) 45.
35. R. I. Ristic, J.N. Sherwood, *J. Phys. D. Appl. Phys.* 24 (1991) 171.
36. Boujhris, et al, *J. Phys: Condensed Matter* 10 (1998) 1621.
37. Sangwal K, Benz K.W, *Prog. Cryst Ggrowth Charact* 32(1996)135-169.
38. Zheng Guo Zong, et al, *cryst.Res.technol* 43(2008) 811-816
39. Guohui Li, et al, *J.Cryst.Growth* 274(2005) 555.
40. P.Rajesh, P.Ramasamy, *Spectrachim.Acta Part A* 74(2009) 210.
41. Dongli Xu and Dongfeng Xue, *Journal of Crystal Growth* 286 (2006) 108-113.
42. P. Rajesh, P. Ramasamy, *Journal of Crystal Growth* 311 (2009) 3491-3497.
43. S. Boomadevi, R. Dhanasekaran, *J. Cryst. Growth* 261 (2004) 70.
44. M. Meena, C.K. Mahadevan, *Cryst. Res. Technol.* 43 (2008) 166.
45. S.Arjunan, et al, *Cryst. Res. Technol.* 43, No 4 (2008) 417-422.
46. K.Uthayarani, et al, *cryst.res.technol.* 43, No.7(2008) 733-739.
47. P.Rajesh, P.Ramasamy, *Physica B* 404(2009)1611-1616.
48. P.Rajesh, P.Ramasamy, *mater.lett* 64(2010)1140-1143.
49. P.Rajesh, et al, *J.Cryst.Growth* 311(2009)1156.
50. P. Rajesh, P. Ramasamy, *Journal of Crystal Growth* 311 (2009) 3491-3497.
51. M.Senthil Pandian, et al, *Mater.Lett* 62(2008)3830.
52. S.Balamurugan, P.Ramasamy, *Mater.Chem.Phys.* 112(2008)1.
53. M. Senthil Pandian, N. Balamurugan, et al, *Mater. Lett.* 62 (2008) 3830.
54. S. Anbukuar, et.al, *mater. Chem. Phys.* 16(1987) 125.
55. G. Anandha Babu, et al, *J. Crystal Growth.* 310 (2008)1228.