Investigation on growth and characterization of 4-phenylpiperazine-1-ium dihydrogen phosphate single crystals

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ABSTRACT *Single crystals of 4-phenylpiperazine-1-ium dihydrogen phosphate (4PPDP) were grown by slow evaporation technique using the mixed solvent of ethanol and water. The reactants used for the crystal growth were phenylpiperazine and orthophosphoric acid. Solubility and metastable zone width for 4PPDP sample were measured at different temperatures. The density of the grown crystal of 4PPDP was measured by floatation method. Single crystal XRD studies were carried out to find the lattice constants and it is ascertained that the sample has the orthorhombic structure. The hardness, work hardening coefficient, yield strength and stiffness constant of 4PPDP crystal were evaluated. The functional groups of the grown crystal were found by FTIR technique. Dielectric constant and loss factor of 4PPDP crystal were measured and the results were analysed. LDT value of 4PPDP crystal were measured using the Nd: YAG laser.*

Keywords: *Semiorganic crystal; solution growth; solubility; XRD; LDT; FTIR; dielectrics; microhardness; phenylpiperazine derivative*

1. Introduction

Organic nonlinear optical (NLO) crystals are more attractive than the inorganic counterparts due to high order of optical nonlinearity, large electro-optic co-efficient with low frequency dispersion, large nonlinear response over a broad frequency range and large structural diversity [1-3]. Inorganic nonlinear optical crystals have high thermal stability and mechanical strength and hence it is necessary to prepare semiorganic NLO crystals and these crystals have both the properties of organic and inorganic crystals. In semiorganic materials
the organic ligand is ionically bonded with inorganic host, because of this, the new semiorganic crystals are having higher mechanical strength and chemical stability and they possess many attractive properties, such as high damage threshold, wide transparency region, high decomposition point, high hardenss and high nonlinear coefficient [4,5]. In this work, a semiorganic NLO crystal viz., 4-phenylpiperazine-1-ium dihydrogen phosphate crystal has been prepared by using phenylpiperazine and orthophosphoric acid. Piperazines are the important group of compounds reported to have diverse biological activity like anthelmintic, antihistaminic, anticancer, antidepressant and hence the present study was undertaken in order to synthesize some piperazine derivatives and evaluate their biological properties. Piperazines are a broad class of chemical compounds with many important pharmacological properties. 1-phenylpiperazine is a simple chemical compound featuring a phenyl group bound to a piperazine ring. Many phenylpiperazines and their derivatives have been synthesized and their properties have been studied by many authors [6-12]. Gurkan Kesan *et al*. have reported spectroscopic studies like FTIR and FT-Raman studies of some metal halides complexes of 1-phenylpiperazine [13]. Manel Essid *et al*. have solved the crystal structure of 4-phenylpiperazine-1-ium dihydrogen phosphate and reported in the literature [14]. As no other physical and chemical properties of 4-phenylpiperazine-1-ium dihydrogen phosphate crystals have been reported in the literature except the crystal structure, the various properties such as spectral, mechanical, electrical properties of the title compound have been carried out for the first time and discussed in this paper.

2. Synthesis and crystal growth of the title compound

The title compound 4-phenylpiperazine-1-ium dihydrogen phosphate (4PPDP) was synthesized by mixing analar grade 1-phenylpiperazine and orthophosphoric acid in the molar ratio of 1:1 by solvent evaporation technique. Here the mixed solvent of ethanol and double distilled water of equi-volume ratio

was used as the solvent for synthesizing 4PPDP salt. The calculated amounts of the reactants were thoroughly dissolved in double distilled water and stirred well for about 2 h using a magnetic stirrer to ensure uniform concentration throughout the entire volume of the solution. Then, this solution was filtered twice and taken in a broad vessel for formation of 4PPDP sample. The synthesized compound was further purified by successive re-crystallization process. It is observed that some small crystals of 4PPDP have been formed in the vessel and these crystals have been used as the seed crystals for grown big-sized crystals. The seed crystals were immersed in the saturated solution of 4PPDP in a growth vessel covered with perforated sheets. Due to slow evaporation, seed crystals were turned into big-sized crystals of 4-phenylpiperazine-1-ium dihydrogen phosphate. The harvested crystal of 4PPDP is shown in the figure 1.

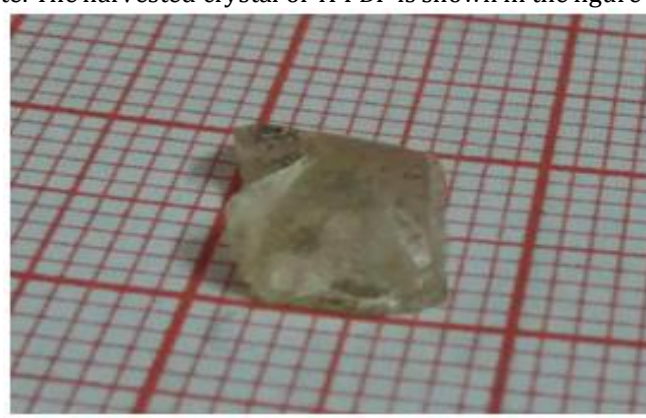

Fig.1: Grown crystal of 4-phenylpiperazine-1-ium dihydrogen phosphate

3. Results and discussion

3.1 Single crystal XRD studies

Single crystal X- ray diffraction studies has been performed by using ENRAF NONIUS CAD4 diffractometer with Mo K_α radiation (λ= 0.71073 Å) at room temperature to find the lattice cell parameter values of 4PPDP crystal. A good quality crystal of 4PPDP was used for the single crystal study. The refinement method used was full matrix least square method. The obtained lattice parameters and data in connection with the single crystal XRD method are provided in the table 1. From the results, it is observed that the grown crystal of 4PPDP crystallizes in orthorhombic crystal structure. The number molecular formula units per unit cell is found to be 4. The space group of this crystal is observed to be $P2_12_12_1$ and this is a non-centrosymmetric space group. The lattice constants of 4PPDP crystal found in this work are observed to be in good agreement with the reported values [14].

Table 1: Single crystal XRD data for 4-phenylpiperazine-1-ium dihydrogen phosphate crystal

Diffractometer	ENRAF NONIUS CAD-4
Radiation	MoK_α,
wavelength	0.71069 Å
Refinement method	Full matrix least square method
Crystal nature	Transparent
Temperature	293(2) K
Symmetry	Orthorhombic
a	6.182 (4) Å
b	8.279 (2) Å
c	24.413 (3) Å
α	90°
β	90°
γ	90°
Z	4
Volume of the unit cell	1249.46(4) $Å^3$
Space group	$P2_12_12_1$
Molecular weight	260.24

3.2 Density measurement

Density of crystals can be found by floatation method. In this method, a high density liquid and a low density liquid are necessary. The liquids used in this experiment are xylene (density: 0.89 g/cc) and carbon tetrachloride (density: 1.59 g/cc). After mixing the liquids xylene and carbon tetrachloride in a suitable proportion in a specific gravity bottle, a small piece of the crystal was immersed in the mixture of the liquids. When the sample was attained in a state of mechanical equilibrium, the density of the crystal would be equal to the density of mixture of liquids. The density was calculated using the equation $\rho = (W_3 - W_1) / (W_2 - W_1)$ where W_1 is the weight of the empty specific gravity bottle, W_2 is the weight of the specific gravity bottle with full of water and W_3 is the weight of the specific gravity bottle full of the mixture of xylene and carbon tetrachloride. By experiment, the density of 4PPDP crystal is found to be 1.392 g/cc. The density was also calculated from the crystallographic data using the relation $\rho = (M.Z)/(N.V)$ where M is the molecular weight of the material used, Z is the number of molecules per unit cell, N is Avagadro's number and V is the volume of the unit cell and by theory, the density of 4PPDP crystal is found to be 1.383 g/cc.

3.3 Measurement of solubility and metastable zone width

Solubility of the crystal is necessary for preparing the saturated and supersaturated solutions at a particular temperature and it gives the information about the amount of the material available for the crystal growth. The solubility for the grown crystal of 4PPDP was determined by gravimetric method. The measurement of metastable zone width (MSZW) was carried out by the polythermal method by using a constant cooling rate to generate supersaturation and the nuclei are detected visually. Saturated solution of 4PPDP has been prepared in accordance with the solubility data. The studies were carried out in a constant temperature bath controlled to an accuracy of + 0.01 ^{o}C provided with a cryostat for cooling below room temperature. A constant volume of 10 ml of solution was used to find MSZW. The solution was preheated to 5^{o}C above the saturated temperature for homogenization. The equilibrium saturated solution is cooled from the overheated temperature and the temperature at which the first visible crystal nucleus formed in the solution is noted and this is the nucleation temperature. This experiment was carried out for the solution saturated at 30, 35, 40 and 45 ^{o}C. Repeated trials were performed to ascertain the correctness of the observed results. The solubility curve and the nucleation curve for 4PPDP crystal are given in the figure 2. It is observed from the results that the solubility increases with temperature and hence the grown crystal of 4PPDP has a positive temperature coefficient of solubility. The MSZW is the difference between the saturation and the nucleation temperatures. The metastable zone width is more in lower temperature region and less in the higher temperature region. Metastable zone width (MSZW) is a basic and an important parameter in terms of temperature for growing a crystal by solution growth technique. The MSZW is strongly influenced by a number of factors such as temperature, measuring technique, nature of solution, pH, mechanical effect and presence of impurities etc [15-17].

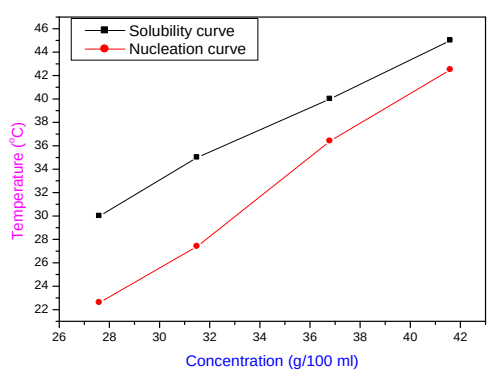

Fig.2: Solubility and nucleation curves for 4-phenylpiperazine-1-ium dihydrogen phosphate

3.4 Mechanical parameters

The hardness and mechanical properties of a crystalline material are closely related to the interatomic bond energy and elasticity of the bonds of the particular plane where the hardness was measured. Load dependence of Vickers microhardness was measured on polished sample. The indentation time was maintained as constant at 10 s. The diagonal lengths of the indented impression were measured for different loads varying from 20 to 100 g. The successive indentations were made at different sites of the

sample surface. Hardness of the material depends on different parameters such as lattice energy, Debye temperature, heat of formation and interatomic spacing. The microhardness studies of 4PPDP crystal were carried out using a Vickers hardness tester. The crystal was mounted properly on the base of the microscope. Now, the selected faces were indented gently by loads varying from 20 to100 g. The length of the two diagonals of diamond indenter was measured by a calibrated micrometer attached to the eyepiece of the microscope after unloading and the average was found out. For a particular load, at least three well defined indentations were considered and the average value (d) was selected. The plot of average indentation length versus the applied load for 4PPDP crystal is shown in the figure 3 and it is noticed that the average indentation length increases with increase of applied load on the surface of the crystal. Using the values of average indentation length, the Vickers microhardness (H_v) number at different loads were calculated using the relation $H_v = 1.8544\ P / d^2$ where P is the applied load and d is the average diagonal length of the indentation. The plot of microhardness number versus applied load for 4PPDP crystal is presented in the figure 4. The increasing value of hardness with increase of load on the surface of the crystal indicates that 4PPDP crystal has the reverse indentation size effect [18, 19]. It is observed that 4PPDP crystal starts damaging when the load applied on the surface of the crystal more than 100 g and crack initiation is observed on the surface.

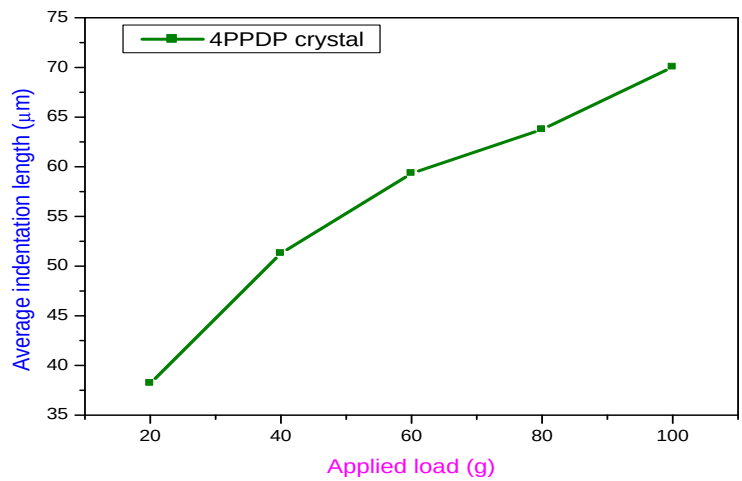

Fig.3: Variation of average indentation length with applied load for 4PPDP crystal

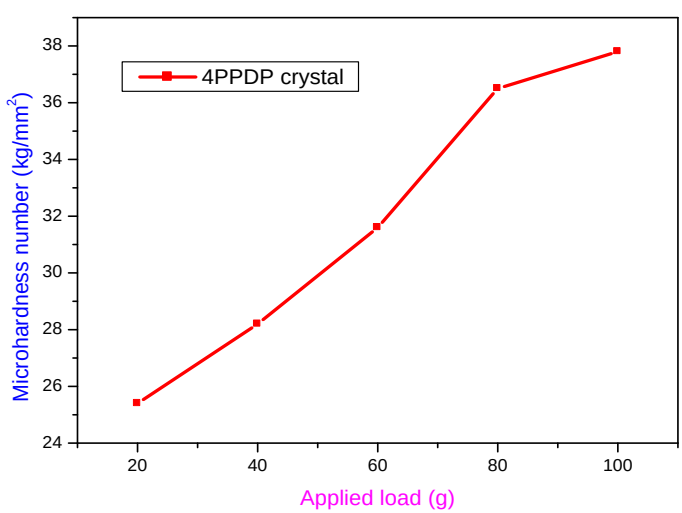

Fig. 4: Variation of hardness number with applied load for 4PPDP crystal

Meyer's law for hardness can be used for checking the material whether it is a soft or hard and this law is given by $P = k_1 d^n$ where k_1 is the material constant, P is the applied load and n is the Meyer's index or work hardening coefficient. If logarithm is taken on both sides of this equation, one gets $\log (P) = \log (k_1) + n \log (d)$. A graph is drawn between log (P) and log (d) and it is shown in figure 5. By best least square fitting method, the slope is obtained and it is equal to the value of work hardening coefficient, which is obtained to be 2.6812. According to Onitsch and Hanneman, 'n' should lie between 1 and 1.6 for hard materials and should be above 1.6 for softer materials. Hence, it is concluded that 4PPDP crystal is a soft material and not the hard material [20, 21]. Other mechanical parameters like yield strength and stiffness constant of 4PPDP crystal were determined using the microhardness data. Yield strength of the crystal can be found out using the relation Yield strength $\sigma_y = (H_v/3)(0.1)^{n-2}$ where σ_y is the yield strength and H_v is the microhardness of the material. The stiffness constant (C_{11}) of 4PPDP crystal was calculated using the Wooster's empirical formula, $C_{11} = H_v^{7/4}$. The calculated values of yield strength and stiffness constant of 4PPDP crystal are given in the table 2. The results indicate that the yield strength and stiffness constant of 4PPDP crystal is high and they increase with increase of the applied load [22, 23].

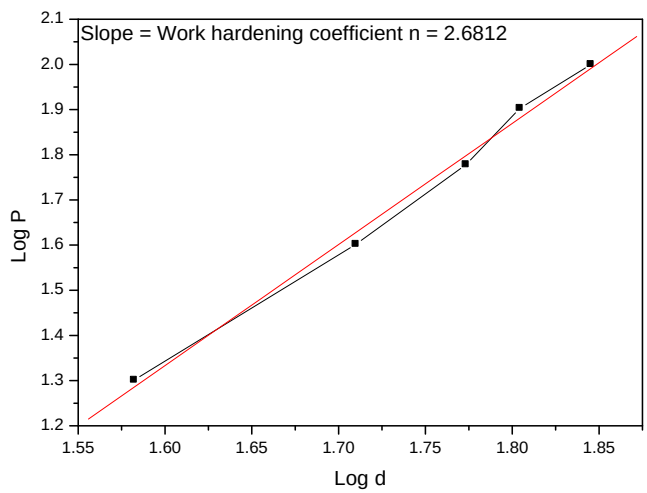

Fig.5: Plot of log (P) versus log (d) for 4PPDP crystal

Table 2: Values of yield strength and stiffness constant of 4PPDP crystal

Applied load (grams)	Yield strength x 10^6 (N/m^2)	Stiffness constant (N/m^2)
20	17.28666	4.93293E+14
40	19.19228	5.92354E+14
60	21.50624	7.22933E+14
80	24.84107	9.30375E+14
100	25.72582	9.89137E+14

3.5 FTIR spectral studies

FTIR spectroscopy is most useful for identifying functional groups of organic and inorganic compounds and it deals with the study of vibrational spectra of molecules. The vibrational frequencies, their relative intensities and shapes of the infrared bands recorded in a double beam spectrometer are used for the qualitative characterization of 4PPDP crystal. An FTIR spectrometer has high resolution, total wavelength coverage, higher accuracy in frequency and intensity measurement compared to that of conventional IR spectrometer. The FTIR spectrum of 4PPDP crystal was recorded using the Perkin-Elmer FTIR spectrometer in the wave number range 400-4000 cm^{-1}. Here KBr pellet technique was adopted for the pelletized sample. The recorded FTIR spectrum of 4PPDP crystal is shown in the figure 6. The peaks at 3854 and 3806 cm^{-1} are due to OH stretching of free water molecules. FTIR spectrum gives the strong absorption broad band in the rang 3200-3000 cm^{-1} is attributed to NH stretching. The absorption peaks at 2760 cm^{-1}, 2482 cm^{-1} are corresponding to CH and CH_2 stretchings. The peaks at 1633 and 1598 cm^{-1} are attributed to the bending of NH. The complete FTIR assignments to the absorption peaks/bands for 4PPDP crystal are

given in the table 3. The FTIR spectral assignments are given in accordance with the data given in the literature [13].

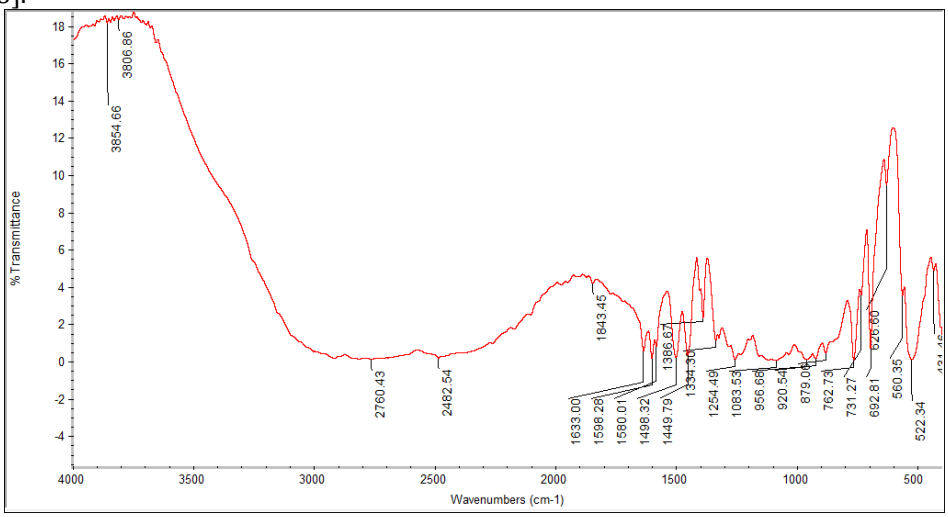

Fig.6: The recorded FTIR spectrum of 4PPDP crystal

Table 3: Assignments for absorption peaks in FTIR spectrum of BAPC crystal

Wave number (cm^{-1})	Assignments
3854	OH stretching of free water molecules
3806	OH stretching of free water molecules
3220-3000	NH stretching
2760	CH stretching
2482	CH_2 stretching
1843	CH_2 stretching
1633	NH deformation
1598	NH deformation
1580	C=C stretching
1498	Ring stretching
1449	CH_2 scissoring
1386	N-C_6H_5 stretching
1334	Ring stretching
1254	CH deformation
956	$(PO_4)^{3-}$ stretching
879	$(PO_4)^{3-}$ stretching
762	CH wagging
731	CH deformation
692	Ring deformation
626	Ring deformation
522	$(PO_4)^{3-}$ stretching
434	NH rocking

3.6 Dielectric parameters

For understanding the electrical behaviour of the crystals, dielectric analysis is one of the characterization studies. The dielectric studies of the grown 4PPDP crystal were measured using an LCR meter in a frequency range 10^2 Hz-10^6 Hz at room temperature. The grown crystal of 4PPDP was polished and coated on either side with silver paste to make a parallel plate capacitor. The values of capacitance with sample and without sample were measured and dielectric constant was calculated. The dielectric loss of 4PPDP crystal was measured directly from the LCR meter. The plots of dielectric constant and dielectric loss versus frequency (log f) for 4PPDP crystal are shown in the figure 7. From the results, it is found that both dielectric constant and loss factor of 4PPDP crystal are high in the low frequency region and these values decrease with increase of frequency. The higher value of dielectric constant in the low frequency region is due to space charge polarization. Generally, the dielectric loss of the material denotes dissipation of

the electrical energy due to electrical conduction, dielectric relaxation, dielectric resonance etc. Here dielectric loss of 4PPDP crystal is highly dependent on the frequency of the applied field and this behaviour is similar to an ionic system [24].

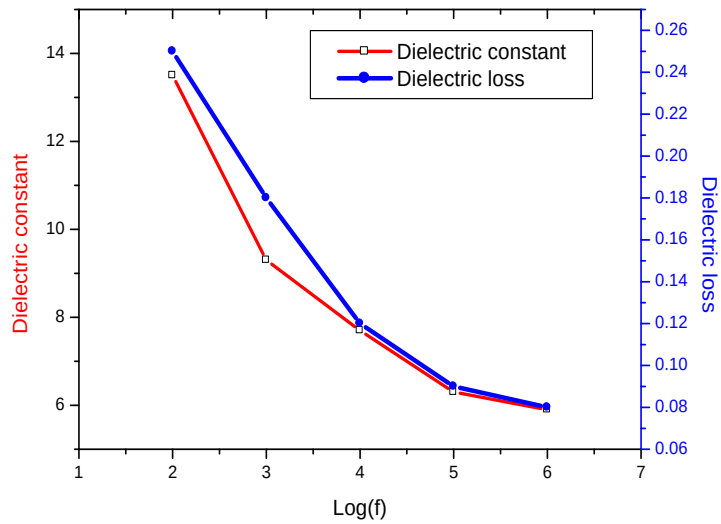

Fig.7: Variations of dielectric constant and dielectric loss versus frequency for 4PPDP crystal

3.7 Laser damage threshold (LDT) studies

Laser light is high intense light and hence a crystal can withstand upto a particular value of input energy of laser light. Beyond this the threshold energy of laser, the crystal starts damaging and cracks may be formed on the surface of the crystal. For NLO crystals, Laser damage threshold (LDT) studies are essential and hence here this study was carried out for 4PPDP crystal using a Nd: YAG laser and the energy of the laser beam was measured by a coherent energy/power meter. The value of LDT is found using the relation P= E/ πr^2 where is the pulse width in ns, E is the input energy in mJ/pulse; r is radius of the spot in mm. The calculated value of LDT for 4PPDP crystal is 0.327 GW/cm^2.

4. Conclusions

The title compound 4-phenylpiperazine-1-ium dihydrogen phosphate (4PPDP) was prepared in the form of single crystals by solution method. XRD study reveals that the grown crystal has orthorhombic structure. The density of 4PPDP crystal was found to be 1.392 g/cc by floatation method. Using microhardness data, the work hardening coefficient of the sample was found to be 2.6812 and also yield strength and stiffness constant were determined. The functional groups like NH, CH, ring stretching, $(PO_4)^{3-}$, OH, CH_2 etc have been identified for the grown crystal of 4PPDP. The dielectric behaviour of the sample was analysed by measuring the dielectric constant and loss factor. Using Nd: YAG laser, the LDT value of 4PPDP crystal was found to be 0.327 GW/cm^2.

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