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RESEARCH ARTICLE

Investigation On Studies Of Urea-Doped Diammonium Hydrogen Phosphate Crystals Grown By Slow Evaporation Technique

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Abstract

Background: To grow single crystals of Urea-Doped Diammonium Hydrogen Phosphate (UDAHP) by solution growth approach with slow evaporation seed immersion technique and to analyze and to discuss the results obtained from different characterization studies. **Methods:** Solution growth method was adapted to grow the crystals of UDAHP using the double distilled water as the solvent. The harvested crystals of UDAHP were subjected to XRD study, FTIR study, microhardness study, UV-visible spectral study, NnonlLinear oOptical (NLO) study, impedance study, LDT study and TG/DTA study. The crystal system and lattice parameters were found by single-crystal X-ray diffraction analysis. Linear optical parameters like transmittance and optical band gap and the mechanical parameters like hardness, fracture toughness, brittleness index, and work hardening coefficient of UDAHP crystal have been estimated. SHG efficiency and LDT values of the sample have been found. **Findings:** By XRD method, the structure of UDAHP crystal is found to be monoclinic structure and the molecular packing diagram of the UDAHP crystal indicates that there are 9 hydrogen atoms, 4 oxygen atoms, 1 phosphorus atom, and 2 nitrogen atoms in a single molecule of UDAHP. Microhardness of the sample is found to be increasing with increase of applied load. Thermal stability of the UDAHP crystal is high and the decomposition point is found to be 195 ^{o}C. The optical band gap of the title compound is 5.75 eV. The value of LDT for urea-doped DAHP crystal is found to be 3.25 GW/cm^2. Relative SHG efficiency of UDAHP crystal is 0.97 times that of the KDP. **Novelty:** The single crystals of uUrea-dDoped dDiammonium hyHdrogen pPhosphate (UDAHP) were grown for the first time. The effect of urea on the properties of Diammonium Hydrogen Phosphate (DAHP) was studied in this work.

Keywords: Single Crystal; Solution Growth; Doping; XRD; Spectroscopy; NLO; SHG; LDT; Microhardness

1 Introduction

Nonlinear Optical (NLO) effect is an interesting effect in which light of one wavelength is transformed to light of another wavelength and NLO crystals have wide range of application in the fields of optical computing, optical communication, laser technology, optical data processing, and photonics [1–4]. Most of the sodium and ammonium phosphates are soluble in water and they are NLO materials [5]. Diammonium Hydrogen Phosphate (DAHP) is an ammonium-based salt that readily loses ammonia upon heating; as a result, it has received little attention at elevated temperatures. Various physical properties of DAHP crystal such as NLO property, thermal property, mechanical properties are interesting for device fabrication [6]. Urea is an organic material exhibiting superior optical, nonlinear refractive index, birefringence, laser damage threshold properties, electrical and hardness properties. Recently, urea and its derivative crystals have been reported in the literature [7–9]. Since urea is an interesting material, it is decided to add urea as the dopant into the host DAHP crystal to alter its various properties. It is to be mentioned here that urea is an organic material and DAHP is an inorganic material and hence in this work, a semi-organic crystal has been grown and studied. Growth, spectral, mechanical, and electrical studies of urea doped NLO crystal have been reported in the literature earlier [10]. In this investigation, the aim of the work is to grow urea-doped DAHP crystal and to study its different properties by carrying out XRD, hardness, NLO, optical, thermal, FTIR and impedance studies and the results from various studies of the title crystal have been discussed in this study.

2 Methodology

2.1 Growth of urea doped DAHP crystals

The solution method with slow evaporation seed immersion technique was used to grow single crystals of urea-doped diammonium hydrogen phosphate (UDAHP) [11]. The salts such as diammonium hydrogen phosphate (DAHP) and urea (99% purity) were purchased from Merck India. To prepare the saturated solution, DAHP salt and urea were combined in a 1:0.05 molar ratio and dissolved in double-distilled water. A magnetic stirrer was used to stir the solution for approximately 3 hours. The solution was then filtered using Whatman filter papers of the highest quality. When the filtered solution is placed in a growth vessel, it reaches supersaturation due to the solvent evaporating. To grow urea doped DAHP in bulk and large sizes, some high-quality seed crystals were placed at the bottom of another growth vessel containing the supersaturated solution. The growth vessel was covered with a perforated polythene paper, and it was kept in a vibration-free stand at room temperature (30°C). As a result of the slow evaporation process, a significant amount of the solute was deposited on the seed crystals, allowing them to grow into large crystals. For the growth of seed crystals and big-sized crystals, it took about 35 days. The photograph of large urea doped DAHP is shown in Figure 1. The size of the crystal is observed to be 20 x 18 x 10 mm^3. The transparent, colourless, and non-hygroscopic nature of the seed crystals and the large crystal observed during the experiment is confirmed. Dopants have been placed into the interstitial sites of the host DAHP crystal to maximise their efficiency because urea is an immobile impurity that is normally deposited at the terrace of the crystal during its development phase.

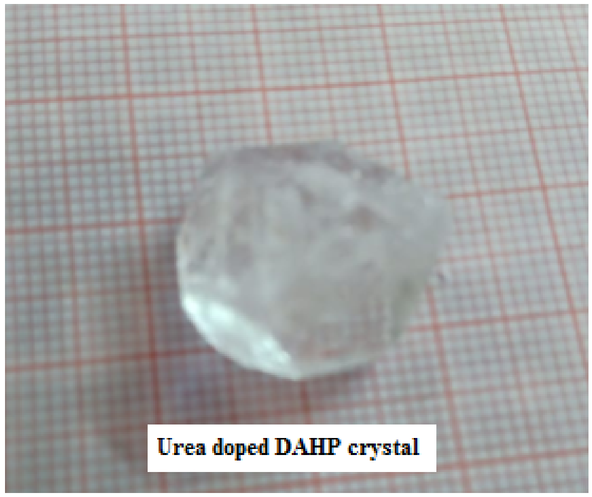

Fig 1. A bulk crystal of urea doped DAHP

2.2 Methods used to characterize the grown crystals

Single crystal XRD study was carried out using a Bruker 4SMART KAPPA APEX II

CCD single-crystal X-ray diffractometer using graphite monochromatized MoKradiation (λ= 0.71073 Å). The UV-vis-spectral study of the title compound were studied using spectrophotometer (Varian, Cary 5000) in the range 190 – 1100 nm [12]. FTIR spectrum was recorded using Perkin Elmer spectrometer in the range of 4000-400 cm^{-1} by the KBr pellet technique. The Thermo Gravimetric (TG) and Differential Thermo Gravimetric (DTA) analyses were done for the grown urea doped DAHP crystal using Perkin Elmer Thermal analyzer at a heating rate from 40 °C to 700°C. SHG study was carried out by Kurtz Perry Powder technique using a Q-switched high energy Nd: YAG laser (Quanta Ray model Lab-170-10) with λ = 1064 nm. The impedance study of the sample was studied by an impedance analyzer model: ZAHNER / Germany – electro chemical work station. Microhardness study of urea doped DAHP crystal was performed by using the SHIMADZU microhardness tester by applying various loads. The thermal curves of the sample were recorded using the SDT thermal analyser (Model No.2960) at the heating rate of 10°C/minute in the nitrogen atmosphere.

3 Results and discussion

Single-crystal XRD analysis

The structure was solved using direct methods and refined using full-matrix least-squares processes utilising the SHELXL programmes. The single crystal XRD data for UDAHP crystal are given in . From the data, it is concluded that urea-doped DAHP crystal crystallizes in a monoclinic structure. Z = 4 is determined to be the number of molecular units in a unit cell. Using the XRD data, the density of the sample crystal has been determined, and the value of density is 1.618 g/cc. The molecular packing diagram of the UDAHP crystal is presented in Figure 2. This figure indicates 9 hydrogen atoms, 4 oxygen atoms, 1 phosphorus atom, and 2 nitrogen atoms in a single molecule of UDAHP and from this diagram, it is confirmed that the unit cell contains four molecules. Since the dopant 'urea' is in the interstitials of the crystal of UDAHP, the positions of urea (in the form of ions) are not revealed by the single-crystal XRD technique.

3.2 Microhardness studies

3.2.1 Microhardness

In a real crystal, hardness depends on the applied load due to the indentation size effect. There are two types of indentation size effects viz. (i) normal indentation size effect and (ii) reverse indentation size effect. The hardness increase with increased

Table 1. Crystal data and structure refinement for urea doped DAHP crystal

1	Identification code	UDAHP
2	Empirical formula	$H_9N_2O_4$ P
3	Formula weight	132.06 g/mol
4	Temperature	296(2) K
5	Wavelength	0.71073 Å
6	Crystal system	Monoclinic
7	Space group	P21/c
8	Unit cell dimensions	a = 10.7498(14) Å, b = 6.6889 Å, c = 8.0120 (11) Å, α = 90o β= 109.784(6)o and γ = 90o
9	Unit cell volume	V = 542.09 (13) Å3
10	No. of molecular units per unit cell (Z)	4
11	Calculated density	1.618 Mg/m3 or 1.618 g/cc
12	Absorption coefficient	0.432 mm-1
13	F (000)	280
14	Crystal size	0.350 x 0.350 x 0.300 mm3
15	Theta range	2.013 to 28.213 deg
16	Limiting indices	-13<=h<=13, -8<=k<=8, -6<=l<=10
17	Reflections collected / unique	4086 / 1279 [R(int) = 0.0218]
18	Completeness to theta	25.242, 100.0 %
19	Max. and min. transmission	0.881 and 0.864
20	Refinement method	Full-matrix least-squares on F^2
21	Data / restraints / parameters	1279 / 0 / 93
22	Goodness-of-fit on F^2	1.099

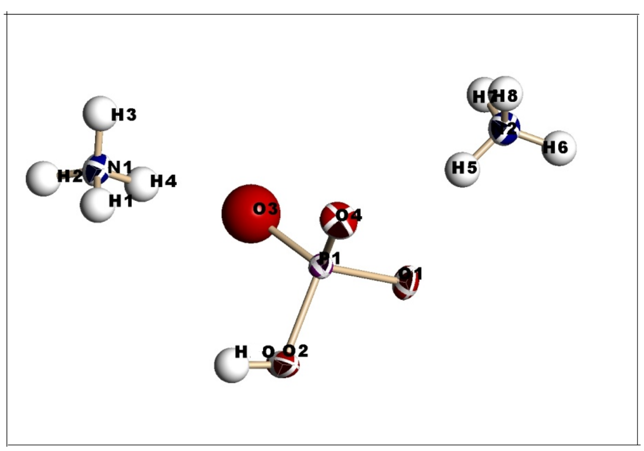

Fig 2. Molecular packing diagram of urea doped DAHP crystal

applied load in a crystal is due to the Reverse Indentation Size Effect (RISE). The decrease in hardness with increasing applied load is due to the normal indentation size effect. It is known that the hardness of an ideal crystal is independent of the applied load. It is reported that some NLO crystals show a normal indentation size effect, and many crystals show a reverse indentation size effect. Also, it is reported that some NLO crystals show both the indentation size effects, and it depends on crystal structure and bonding arrangements[(13)]. Microhardness measurements were conducted on a grown crystal of UDAHP with flat faces that were microscopically free of damage and had approximate dimensions of 5 mm × 4 mm × 3 mm. On the selected crystal, indentations were made using a Vickers microhardness tester. The crystal was mounted on the microscope's base, and the selected face was gently indented with loads of 30 g, 50 g, 70 g, 100 g, 150 g, 200 g, and 250 g for a dwell time of ten seconds. After unloading, the two diagonal lengths of indentation were measured for each applied load using a micrometre mounted to the microscope's eyepiece. The average diagonal length of the indentation (d) was determined. Using the values of d, the Vickers microhardness number (H_v) was determined using the expression $H_v = 1.8544\ P/d^2$ where P denotes the applied load and d denotes the indentation's average diagonal length. Load dependence of the average value of diagonal indentation and load dependence of microhardness for urea doped DAHP crystal are presented in Figure 3. The results indicate that the average value of diagonal indentation (d) increases as the applied load increases. The hardness of this crystal decreases with an increase of load up to 200 g, and then it slightly increases. The decreasing trend of the hardness of the UDAHP crystal reveals that the crystal has a normal indentation size effect of up to 200 g. The increasing trend of hardness in the crystal is due to the reverse indentation size effect. The Reverse Indentation Size Effect (RISE) occurs in urea-doped DAHP crystals that readily deform due to (i) the predominance of dislocation nucleation and multiplication; and (ii) relative dominance of either a set of slip planes of a given slip system or the relative predominance of two slip systems below and above a particular applied load. It is observed that the hardness of urea-doped DAHP crystal is more than that of undoped DAHP crystal.

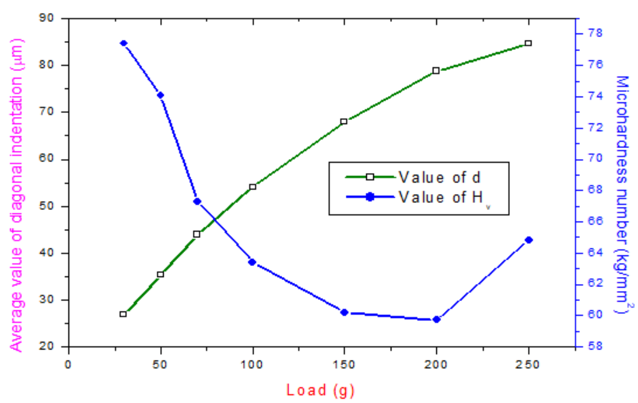

Fig 3. Variation of the average value of diagonal indentation (d) and microhardness number (H_v) with applied load (P) for urea doped DAHP crystal

3.2.2 Meyer's index

The Meyer's index or work hardening coefficient (n) was obtained using the "Meyer's law as given by $P = kd^n$ where k is the resistance of the material to initial penetration and P is load, and this expression was formulated by Eugene Meyer in 1908. Meyer's index is as a measure of the effect of the deformation on the hardness of the crystal"[(14)]. The values of k and n are dependent on the size of the indenter, and hence Meyer's law can also be written as

$P = k_1 d_1^{n1} = k_2 d_2^{n2} = k_3 d_3^{n3}$ .....

Since only one indenter type was used in this work, the first equation can be considered here. By plotting a graph of log(P) against log(d) as given in Figure 4, the slope is obtained, and this is equal to the value of Meyer's index for urea doped DAHP, and the obtained value of n is 2.367. Since this value is more than 1.6, this crystal is found not to be a hard material.

3.2.3 Fracture toughness and brittleness index

Fracture toughness and brittleness index are important mechanical parameters that can be determined using the values of hardness and crack length of indentation. "Fracture toughness is an important mechanical parameter which is the relative degree of resistance to impact without any fracture in the material and it is related with the material enables to absorb energy

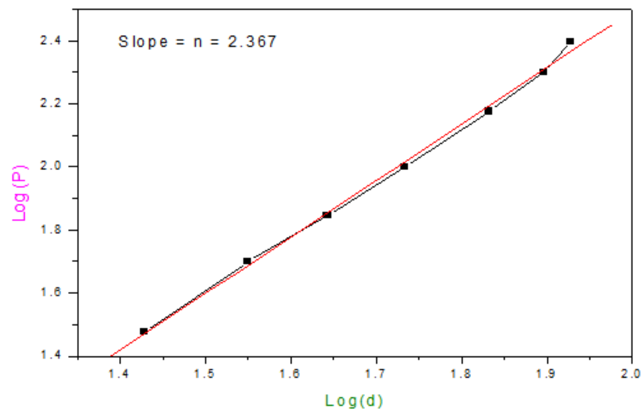

Fig 4. Plot of log (P) versus log (d) for urea doped DAHP crystal

while it is being stressed above its elastic limit"[15]. As a result of indentation, there are two types of cracks: radial-median cracks and Palmqvist cracks. The fracture toughness (K_c) can be estimated using the following expression

In this Where β_o=7 for Vickers hardness indenter, and the value of c is 74 μm for the load of 250 g. The obtained fracture toughness value for urea doped DAHP crystal is 0.056 g/(μm)$^{3/2}$. "Brittleness is another mechanical property of the material, and it is in connection with the fracture without any appreciable deformation". It is measured in terms of brittleness index (B_i) as given by

Where H_v is the Vickers hardness number, the Brittle index of UDAHP crystal is 1.161 μm$^{-1/2}$ for the applied load of 250 g .

3.3 UV-visible spectral studies

Since low intense ordinary UV and visible light are used to record transmittance spectrum, the estimated parameters from UV-visible spectral studies are linear optical parameters. Transparency, absorption coefficient, bandgap, extinction coefficient, refractive index, and optical conductivity are all significant linear optical properties of a crystal. The optical properties of crystals are determined by the interaction of the crystal with the electromagnetic waves electric and magnetic fields. The UV-visible transmittance spectrum of urea doped DAHP crystal was recorded and it is shown in Figure 5. The lower cut-off wavelength of the sample is 215 nm, and the transmittance is high in the visible region. The appearance of the absorption peak at 281 nm is due to the doping of urea into the lattice of the grown crystal. The absorption coefficient (α) obeys the following relation for photon energy (hν).

where E_g is the optical bandgap of the crystal and A is a constant[16]. The above expression is referred to as Tauc's relation, and the plot created with it is referred to as Tauc's plot Figure 6. The value of the exponent 'n' represents the nature of the transition; for example, n= $\frac{1}{2}$ for indirect transitions and n=2 for direct transitions. From Tauc's plot, the optical bandgap of the grown crystal is found to be 5.75 eV.

3.4 Thermal studies

Thermal studies for the grown urea doped DAHP (UDAHP) crystal were carried out by recording ThermoGravimetric (TG) and Differential Thermal Analysis (DTA) curves. Thermogravimetric analysis is the process of determining the weight of the sample under investigation as the temperature increases at a predetermined rate. DTA is the measurement of the temperature difference between a sample and a reference sample when the system is heated. The recorded TG/DTA thermal curves are presented in Figure 7. From the results, it is seen that the sample is thermally stable up to 195 °C. TG curve has three stages: (i) the first stage covers the temperature range 50-195 °C, and in this stage, the sample is thermally stable, (ii) the temperature. The range for the second stage is 195 – 420 °C, and in this stage, decomposition of the sample occurs, and the decomposition point of the sample is 207 °C and (iii) the third stage is from 420-700 °C. In this stage, the weight percentage of the sample is about 50%, and it remains almost constant. The DTA curve shows an endothermic at 207 °C, and it seems that there is no significant exothermic peak. From the thermal curves, it is ascertained that there is no water molecule in the UDAHP crystal[17].

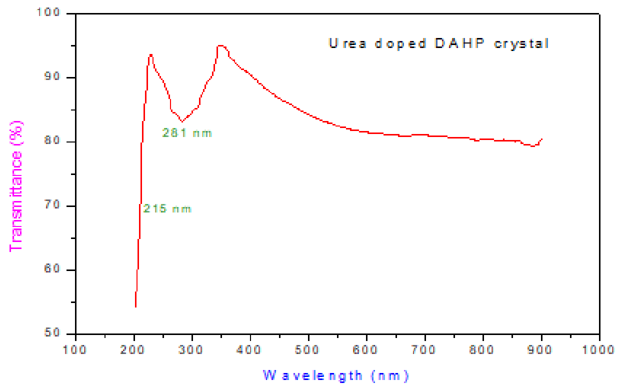

Fig 5. UV-visible transmittance spectrum of urea doped DAHP crystal

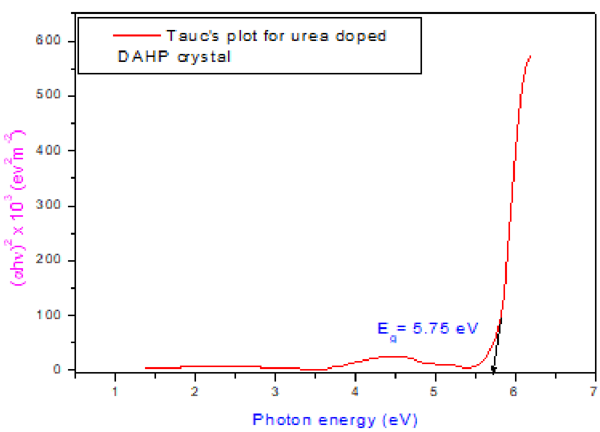

Fig 6. Tauc'splot for urea doped DAHP crystal

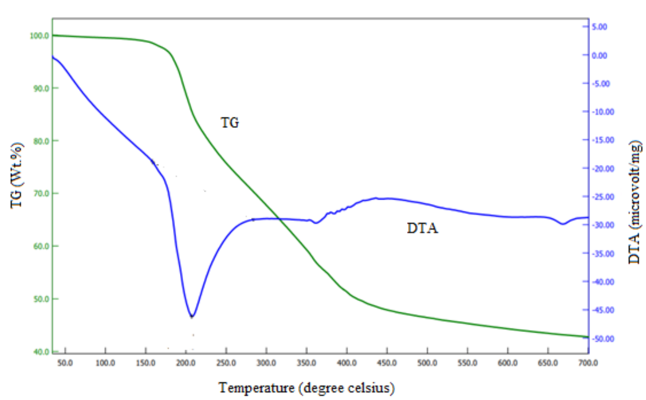

Fig 7. TG/DTA curves for urea doped DAHP crystal

3.5 Electrical impedance

A dielectric material is known to be storing electrical energy, which can be understood by impedance analysis. The impedance is a complex quantity, and it can be written as Z* = Z'- jZ" where Z' denotes the real part of impedance and Z" denotes the imaginary part of impedance. The grown crystal was pelletized, and the measurement of impedance was performed at 30 °C and 60 °C. A Nyquist plot is drawn by taking the real part of impedance (Z') along the X-axis and the imaginary part of impedance (Z") along the Y-axis at various frequencies. The obtained Nyquist plots for the sample are shown in Figures 8 and 9 and these plots give ideas of the presence of bulk effect and grain boundary effect of the crystal. Semicircles in the high-frequency region indicate both the effects [18].

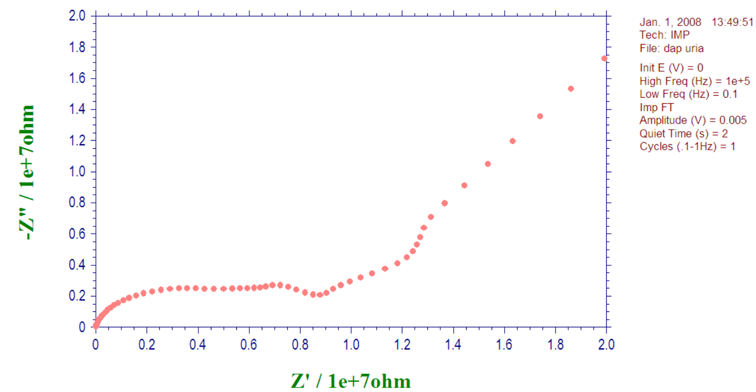

Fig 8. Nyquist plot of urea doped DAHP crystal at 30° C

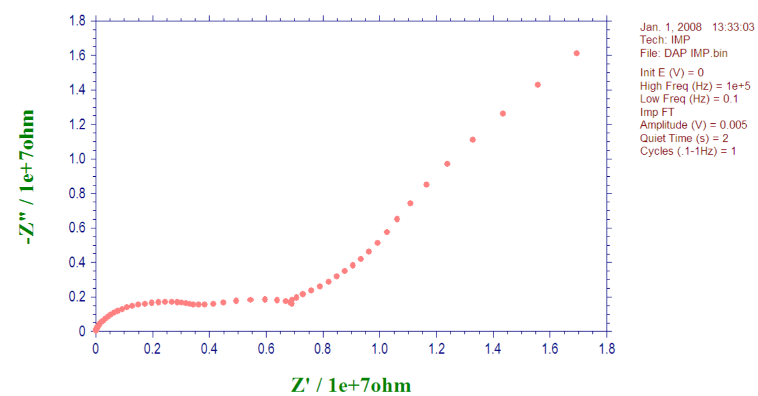

Fig 9. Nyquist plot of urea doped DAHP crystal at 60° C

3.6 Laser damage threshold value

Since large laser power is used in NLO crystals for SHG, THG, and optical parametric phenomena, laser damage threshold (LDT) is an important parameter to be measured. It is known that LDT value in optical materials remains the limiting factor in the development of laser systems and NLO devices. Here, using a Q-switched Nd: YAG laser (Continuum USA, Model: Surelite-III) of wavelength 1064 nm and pulse width 10 ns, the value of LDT of urea doped DAHP crystal was measured. The occurrence of single-pulse damage was observed by tracing the fall in transmitted intensity detected by a fast PIN type Si-photodiode and traced in a digital storage oscilloscope, which was used to detect the damage. "The value of LDT was estimated using the formula $P = E/\pi\tau r^2$, where E is the input energy in mJ/pulse, τ is the pulse width, and r is the radius of the laser spot" [19]. The evaluated value of LDT for urea-doped DAHP crystal is 3.25 GW/cm^2. It is observed that this value of LDT is high, and hence the grown crystal can be applicable in high power opto-electronic devices and other NLO applications.

3.7 Second harmonic generation (SHG

Among second-order NLO phenomena, second harmonic generation (SHG) is an important process because it creates frequency doubling in non-centrosymmetric crystals. The relative SHG efficiency was measured by using the experimental set-up of the Kurtz-Perry powder method. The grown crystal of urea-doped DAHP crystal was crushed into fine powder. The particle size of the sample was estimated to be 250-300 μm by using a good quality sieve. The reference sample used in this experiment was KDP, and the particle size of the KDP powder sample was kept the same as that of the UDAHP sample. The samples were subjected to laser radiation from a Q-switched Nd: YAG laser of the wavelength of 1064 nm. The emission of green radiation from the samples gives an indication of frequency doubling. The energy of the emitted radiation was measured by using the power meter. The results show that the SHG efficiency of urea-doped DAHP crystal is 0.97 times that of the KDP crystalline sample, and this value is observed to be slightly more than that of undoped DAHP crystal.

3.8 Identification of functional groups

The functional groups of urea-doped DAHP crystal have been identified by carrying out FTIR studies. Fourier transform infrared (FTIR) spectral study is particularly useful for studying molecules, finding stretching modes, bending or deformation modes of the sample[20]. The FTIR spectrum of the sample was recorded an FTIR spectrometer in the range of 500–4000 cm^{-1}, and it is presented in Figure 10. The broad envelope between 3600 and 2950 cm^{-1} is due to stretching OH and NH modes. The absorption peak at 1664 cm^{-1} corresponds to NH bending mode, and the peak at 1622 cm^{-1} is assigned to OH bending mode. The peak at 1455 cm^{-1} is due to NH_2 bending, and P-O stretching appears at 1385 cm^{-1}. The peak at 1079 cm^{-1} is given C-O stretching mode. The peaks in the fingerprint region at 785 and 534 cm^{-1} correspond to PO_4^{3-} stretching and PO_4^{3-} deformation modes, respectively.

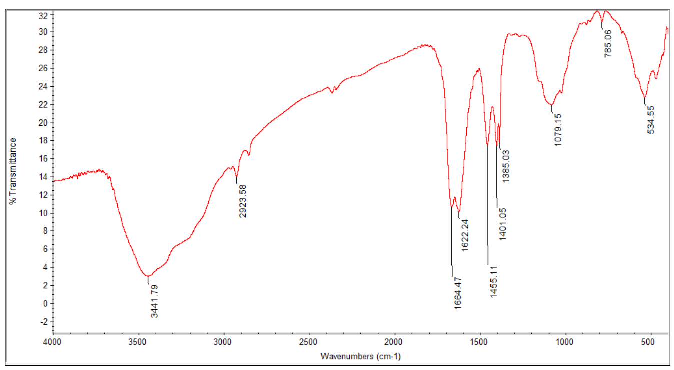

Fig 10. FTIR spectrum of urea doped DAHP crystal

4 Conclusions

Single crystals of urea-doped DAHP crystals were grown using a solution method combined with a slow evaporation technique. The crystal structure of the sample was identified as monoclinic, and it is found that the crystal structure of the sample has not been changed due to the doping of urea into DAHP crystal. The nonlinear behaviour of hardness, work hardening coefficient, and other mechanical parameters of the sample have been analyzed. The optical band gap of urea doped DAHP crystal was found to be 5.75 eV, and other linear optical parameters of the sample have been discussed. The functional groups of the sample such as NH, NH_2, P-O, C-O, and PO_4^{3-} have been identified. LDT value of urea doped DAHP crystal was evaluated. The relative SHG efficiency of urea-doped DAHP (UDAHP) crystal is found to be 0.97 times that of the KDP. The value of LDT for urea-doped DAHP crystal is estimated to be 3.25 GW/cm^2 and this is found to be a high value. It is ascertained that the impedance of urea-doped DAHP crystal decreases as the temperature increases. From TG/DTA studies, it is observed that UDAHP crystal is thermally stable up to 195 °C. Since hardness, SHG efficiency, transmittance, LDT and thermal stability of urea doped DAHP (UDAHP) crystal are more than undoped DAHP crystal, UDAHP crystal can be used as a good candidate for NLO applications.

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