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Synthesis, Growth, Structural and Optical Studies of Nonlinear Optical Material- Piperazine1,4-Diium Bis Dihydrogen Phosphate.

Chemistry

KEYWORDS : Crystal structure, X-ray diffraction, Growth from solution, Single crystal growth, Non-linear optics.

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ABSTRACT

Piperazine 1,4 diium bis dihydrogenphosphate is one of the useful materials with nonlinear optical (NLO) property to find applications in the fields of optoelectronics and photonics. The material was grown by slow evaporation solution growth method at room temperature. The crystal system and lattice parameters were determined using single crystal XRD analysis. The grown material crystallizes in triclinic system with P-1 space group. The various functional groups were identified using FTIR analysis. The optical properties of the crystal were studied by UV-vis-NIR spectroscopy. The Second Harmonic Generation (SHG) of the crystal was tested to confirm the nonlinear optical property.

Introduction

Second order non-linear optical (NLO) crystals are widely used to convert the frequency of coherent laser sources. Laser based imaging communications like remote sensing, optical data storage and optical computing, optoelectronics and counter measure systems require NLO materials with enhanced activity to accomplish such conversion [1,2]. The widest search for new compounds and crystals led to the development of many amines - based single crystals.

Piperazine is the most important building block in today's drug discoveries [3]. Piperazine citrate is well known antihelmenting drug. Organic phosphate complexes have been widely studied due to their numerous practical, potential and pharmaceutical uses in various fields such as bimolecular sciences, catalysts, fuel cell, liquid crystal material developers and quadratic non-linear optics [4,5,6].

There is an increasing demand for single crystals for their applications in the development of technology and devices for their NLO property. Therefore, in the present investigation, the title compound piperazinium 1,4-diium bis dihydrogen phosphate was grown first as a single crystal using slow evaporation technique. The growth of the crystal was followed by detailed characterization studies such as single crystal XRD study, UV-vis-NIR and FTIR spectral studies and SHG study to analyze structural property, transmission range, identification of various functional modes and NLO property of the grown material.

2. Experimental Procedure

2.1. Material synthesis

Single crystals of Piperazine-1,4-diium bis dihydrogen phosphate were grown by slow evaporation solution growth method at room temperature. Piperazine and orthophosphoric acid were dissolved with 1:1 molar ratio in deionized water to get a clear solution and the solution was stirred well for homogeneity. The resulting solution was filtered using a Whattman filter paper and the beaker containing the filtrate was kept in a dust free environment for crystallization. After a period of 25 days, the title material was obtained with more transparency. The purity of the synthesized crystal was improved by successive recrystallization process. Fig.1 shows the as-grown single crystal of the title compound with dimension of 20x15x18 cm^3.

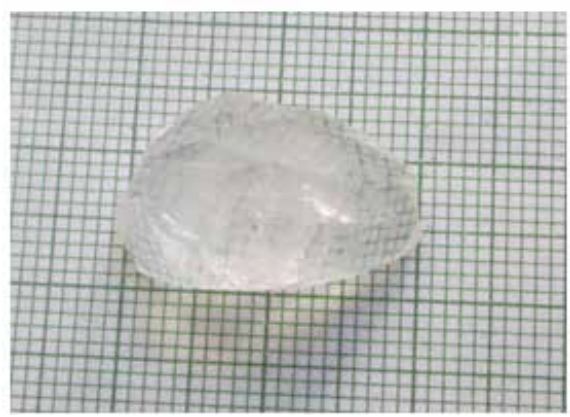

Fig.1 As grown crystal of the title compound

3. Single crystal XRD analysis

Single crystal X-ray measurements were made using a Enraf Nonius CAD4-MV31 X-ray diffractometer. The crystal structure was solved by a direct method

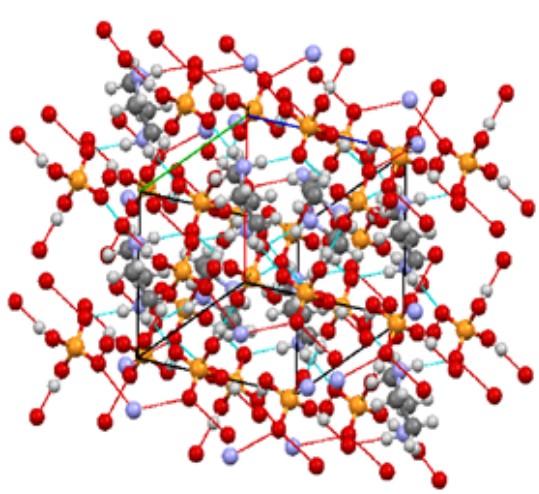

Fig.2 Packing diagram of the atoms present in the grown crystal.

single crystal XRD data collection, 8,232 reflections were recorded in the range of 1.70° to 24.97° of which 2036 reflections were unique reflections. It has been found that the synthesized crystal belongs to the triclinic crystal system with space groupP-1.The lattice parameters obtained are a=7.0367(9) Å, b=7.7140 (13) Å, and c=12.0975(16) Å; α=84.506(7)°, α=81.491(5)° and α=63.023(4) °. The unit cell volume is 578.47(14) $Å^3$ and Z=1.Since the grown crystal is a new compound (CCDC no.1026618), the crystallographic data of this compound are not available in the literature to confirm the results.

The crystalline packing (Fig.2) shows piperazinium cations to be interposed between two centrosymmetric pairs of dihydrogen phosphate anions. The anion pairs are hydrogen bonded (N-H...O) to the cations and the motif is connected to its b-translation equivalents to form a one dimensional hydrogen bonded chain parallel to b-axis. The single crystal X-ray structure of the proton transfer complex of the title compound shows the presence of protonated piperazine cation and deprotonated dihydrogen phosphate anion for intermolecular hydrogen bonding associations as shown in packing diagram.

The detailed geometries of H2P(1)O4- and H2P(2)O4- entities show that the P···O distances significantly are shorter [1.5033 (13) to1.5144 (13) A°] than the P···OH distances [1.5575 (13) to 1.5732 (13) A°], which is in full agreement with those observed in such anions in other organic dihydrogen phosphates. The average of the P···O distances and the O—P—O angles are 1.5088 (13) Å and 113.35(8)°, respectively. They agree perfectly with that generally observed for anions in other phosphates. The O—P—O angles spread in the range 103.24 (7) -114.21 (8)°. The smaller ones 103.24 (7)° and 107.78 (8)°, are related to the HO—P—OH angle. All these geometrical parameters are in full agreement with those observed in such anions in other organic dihydrogen phosphates ,which is probably due to the presence of two acidic hydrogen atoms on the P—O leading to the formation of strong hydrogen bonds. Furthermore, the short P—P distance is in favour of the general formation of polyanions[H2PO4-]nn- in the crystal structure, but not to the individualization of the H2PO4-groups [9,10].

4. FTIR analysis

The FTIR spectrum of the title compound was recorded using JASCO FT-IR 410 spectrometer by the KBr pellet method. The characteristic absorption bands were recorded in the spectral range 4000-400 cm^{-1} in order to confirm the presence of functional groups in the crystal. The presence of P-OH, N-H and C-H is confirmed with the assigned wave numbers from the spectrum.The 3248 cm^{-1} and 3020 cm^{-1}absorption peaks are due to N-H asymmetric stretching and symmetric stretching vibrations. The absorption peaks at 2822 cm^{-1} and2415 cm^{-1} are due to C-H asymmetric stretching and symmetric stretching vibrations.. The lower peaks at 867 cm^{-1} and 775cm^{-1} are due to asymmetric stretching and symmetric of PO_4 stretching modes while 543 cm^{-1} are due to PO_4 bending modes [11,12].

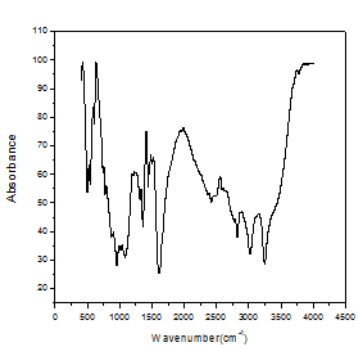

Fig .3 FT-IR spectrum of grown crystal.

5. UV-vis- NIR spectral analysis

The UV-vis-NIR absorption spectrum of the grown crystal was recorded using Perkin-Elmer Cary 5E spectrometer in the wavelength range of 200-1400 nm (Fig.4). The higher intensity of the absorption band observed in the UV region may be due to conjugated systems present in the grown material. The absorption is found to be very low near infrared region and the entire visible region with cut-off wavelength 400nm. The optical band gap (Eg) was evaluated using Tauc's relation given by $\alpha h\alpha = A(E_g - h\alpha)^2$

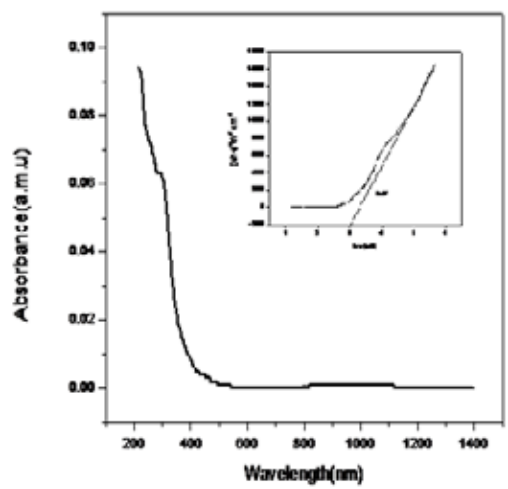

Fig.4 UV-Vis-NIR spectrum of the grown crystal

where A is a constant, E_g is the optical band gap, h is the Planck constant and ν is the frequency of the incident photons. The value of band gap energy was estimated from the graph between $(\alpha h\nu)^2$ and $h\nu$ (inset of Fig.4) by extrapolating the linear portion of the curve to zero absorption. The optical band gap was measured as 3 eV. The higher value of optical band gap suggests that material is dielectric in nature. Only the dielectric material will have wide transparency. The material with wide transparency is required for the fabrication of optical devices.

4.8 SHG efficiency measurements

The SHG efficiency of the grown crystal was measured by modified Kurtz and Perry technique using Nd: YAG laser with pulse repetition rate of 10Hz and wavelength 1064 nm. The sample was ground well and tightly packed in a micro capillary tube. The relative SHG efficiency of the grown crystal was measured by comparing the SHG output with the help of a standard KDP (Potassium dihydrogen phosphate) sample of same particle size. The relative efficiency was found to be 1.5 times that of standard KDP and SHG was confirmed by the emission of green radiation (532nm) from the crystal.

In the grown crystal, the strong proton donor orthophosphoric acid transfers a proton to the strong proton acceptor piperazine. Intermolecular hydrogen bonding is formed between the hydrogen of the protonated nitrogen atom of piperazine and the negatively charged oxygen atom of the dihydrogen phosphate anion. In the present case, the donor–acceptor strength is considerably high due to the intermolecular hydrogen bonding. The NLO behaviour of the title compound may be due to the presence of intermolecular hydrogen bonding. This indicates that the synthesized crystal can be used as a better NLO material.

5. Conclusion

Single crystals of Piperazine-1,4-diium bis dihydrogen

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phosphate were synthesized and crystallized using piperazine and orthophosphoric acid as starting materials by slow evaporation method. The structure of the grown crystal was solved using SHELXS-97 program. It is observed from the crystallographic data that the grown crystal belongs to triclinic system with P-1 space group. The high value of optical band gap and the wide transmission range were ascertained using UV-vis-NIR spectrum. The presence of various functional groups and present in the grown crystal was confirmed by FT-IR spectral analysis. The crystal possesses SHG efficiency 1.5 times higher than that of KDP. Therefore, the grown useful single crystal is a useful organic crystal with NLO applications.

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