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Synthesis, Growth and characterization of a semi organic non linear optical crystal: Piperazine Di-orthophosphate

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1.Introduction

The design and characterization of organic crystals having second order nonlinear optical property have become hot spot for chemistry and physics researchers due to their potential applications in the area of telecommunications, signal processing, optical switching and data storage technology [1-3]. The properties of organic compounds relevant to non linear optics can be refined using molecular engineering and chemical synthesis [4]. The main advantages of organic materials are that their structure can be modified to get the desired NLO properties [5, 6]. Moreover, it has been demonstrated that organic crystals have large nonlinear susceptibilities compared with inorganic crystals. Particularly, amino acid family crystals are of great interest due to their attractive nonlinear optical properties [7]. When the organic acid is mixed with an amino acid, NLO property has been increased due to the zwitter ionic nature and high transparency range [8, 9]. Piperazine is one such amino acid with higher SHG efficiency.

In the present work Piperazine di-orthophosphate was grown by slow evaporation technique and the grown crystals have been subjected to X-ray diffraction, Fourier transform infrared spectral analysis, optical absorption, thermal and second harmonic generation efficiency studies.

2. Experimental

2.1 Synthesis and Growth

Piperazine di-orthophosphate was synthesized from Piperazine and orthophosphoric acid in the ratio of 1:2. The selection of solvent is important for the growth of good quality crystals. The calculated amount of Piperazine and orthophosphoric acid was dissolved in a mixed solvent of acetone and water.

ABSTRACT

Optical quality single crystal of Piperazine di-orthophosphate (PDOP) has been synthesized and grown by slow evaporation solution growth technique. Single crystal X-ray diffraction study reveals that the crystal belongs to triclinic system with space group P-1. The powder X-ray diffraction spectrum was recorded and the peaks were indexed. UV-Vis absorption spectrum shows that the crystal is transparent in the entire visible region. The functional groups present in the material were interpreted by FTIR spectral analysis. Thermal analysis carried out on the compound reveals that the sample is stable upto 160° C. The second harmonic generation efficiency of the title material is 0.85 times higher than that of the standard KDP crystal.

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The reactants were stirred well for two hours using a temperature ontrolled magnetic stirrer to yield a homogenous mixture of the solution. The prepared solution was allowed to evaporate under room temperature. The product was recrystallized twice to remove the impurities. The transparent crystals obtained in a period of 15 days are shown in Fig.1.



Fig 1. As-grown crystals of Piperazine di-orthophosphate. 3. Results and Discussion

3.1. Single crystal X-ray diffraction

Single X- ray diffraction studies of PDOP were carried out using CADENTRAF NONIUS X- ray diffractometer with MoK_{α} ($\lambda = 0.7107$ Å). The crystal belongs to triclinic system with space group P-1. The cell parameters are a= 7.0185 Å, b= 7.6632 Å, c= 12.0865Å, and volume V = 650.02 Å³.

3.2 Crystal Structure determination

X-ray crystallographic studies were carried out using a CADENRAF NONIUS X-ray diffractometer with MoK radiation ($\lambda = 0.71073$ Å) controlled by a Pentium-based PC running the SMART (version 5.05, 1998). Single crystals were mounted on glass fibers at room temperature, and data were

collected at room temperature (20° C). The structure solution and refinement were performed using SHELXTL. The structure was solved by direct methods and full-matrix least-squares refinements using F^2 taking all the unique reflections. The crystal data, experimental conditions and structure refinement parameters are presented in Table 1. All the non-hydrogen atoms were refined with anisotropic thermal parameters. The H atoms which participated in the H-bonds were located from the difference Fourier and refined with isotropic thermal parameters. All the other H atoms (-CH) were positioned geometrically and refined using a riding model with C-H = 0.97 (-CH) or 0.98 (-CH₂) Å with U_{iso} (H) = 1.2 U_{eq} (parent C atom). Single crystal X-ray diffraction analysis shows that the crystal crystallizes in centrosymmetric triclinic crystal system with space group P-1. The ORTEP diagram and crystal packing are shown in fig.2 and fig.3 respectively. The unit cell contains two molecules of phosphoric acid and piperizone each. Phosphoric acid and piperizone are stabilized by hydrogen bonds such as N-H-O and O-H-O with number of short contacts. The two piperizone molecules are tilted at an angle 27.57° with the mean distance between the two phosphorous atoms at 4.692Å. The C-N bond distance is in the range 1.478 to 1.480 Å while the bond length between the adjacent C-C bond in the piperozone molecule varies from 1.498Å





Powder X-ray diffraction analysis has been carried out using Rich Seifert X-ray diffractometer with CuKa ($\lambda =$ 1.5418Å) line radiation. The sample was scanned over the range 10°–60° at a rate of 1°/min. The X-ray diffraction pattern of PDOP is shown in Fig.4. The X– ray diffraction peaks were indexed for the lattice parameters. The prominent peaks in the powder X-ray diffraction confirm the crystalline nature of the grown crystals. The peak corresponding to (120) has maximum intensity per second.

Table 1. Crystal data and structure refinement	
Empirical formula	C4 H16 N2 O8 P2
Formula weight	282.13
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 6.9935(3) Å
	b = 7.6602(4) Å
	c = 12.0249(6) Å
	$\alpha = 84.428(3)^{\circ}$
	$\beta = 81.516(2)^{\circ}$
	$\gamma = 62.883(2)^{\circ}$
Volume	566.78(5) Å3
Z	2
Density (calculated)	1.653 mg/m3
Refinement method	Full-matrix least-squares on F2
Final R indices	R1 = 0.0260
[I>2sigma(I)]	



Fig 4. X-ray diffraction pattern of PDOP crystals. 3.4 Morphology

Morphology predicts the external shape of a crystalline material from its internal crystal structure. The relationship between the crystal morphology and the internal arrangement of atoms in the crystal is therefore of great interest to chemists, chemical engineers, and process engineers. Rationalization of this relationship allows the prediction of crystal shape, the development of tailor-made additives, and the control of solvent and impurity effects. One can study the morphology to study the shape and to consider the effects of altering the growth rate of particular faces on crystal shape.

The morphology of PDOP single crystal was determined by contact goniometry [10] and is depicted in Fig.5. For indexing the crystal surfaces, the crystal was mounted on a four circle goniometer. Reflections from few planes were collected using Enraf CAD-4 diffractometer. The morphology studies indicate that the prominent planes are (-2 0-3), (1 1 0), (0 1 1), (2 1 1), (0 0-1) and (1 1-1). The (0 1 0) plane is the most prominent plane among the other well developed planes.



Fig 5. Single crystal morphology of Piperazine diorthophosphate.

3.5 FTIR Analysis

The FTIR spectrum of PDOP was recorded using the Bruker IFS 66V model FT-IR spectrometer in the wave number range 400–4000 cm⁻¹. The absorption peaks due to the vibrations of various functional groups present in the material was interpreted using Fig. 6. The C=C symmetric stretching is observed at 1633 cm⁻¹. The C-C ring appears at 1500 cm⁻¹. The sharp peak at 1462 cm⁻¹ corresponds to C-H bending. The peak at 1383 cm⁻¹ is assigned to N-O symmetric stretching. The C-O symmetric stretching appears at 1301 cm⁻¹. The C-H bending is observed at 973 cm⁻¹. The peaks at 612 cm⁻¹ and 601 cm⁻¹ are attributed to SCN stretching. The COO rocking appears at 548 cm⁻¹. The C-N out of plane bending is observed at 512 cm⁻¹.



Fig.6. FTIR Spectrum of Piperazine di-orthophosphate single crystals

3.6. UV-Vis-NIR absorption spectrum

The grown single crystal with was subjected to UV-vis-NIR studies at room temperature in the wavelength range from 400 to 1200 nm using a Shimadzu UV-vis spectrophotometer and the recorded spectrum is shown in Fig 7. From the absorption spectrum, it was found that the lower cut-off wavelength is 380 nm. At low frequencies, the crystal absorbs UV light, however, the crystal is found to be transparent in the region of 400-900 nm which is an essential parameter for frequency doubling applications [11].



Fig 7. UV-Vis-NIR absorption Spectrum of Piperazine diorthophosphate

3.7. NLO studies

The NLO property of the powder sample was confirmed by the Kurtz and Perry powder technique [12]. A Q-switched Nd-YAG laser beam of wavelength 1064 nm was used with an input power of 2.0 mJ and pulse width of 10 ns, the repetition rate being 10 Hz. The SHG behavior is confirmed from the output of the laser beam having the bright green emission (λ =532 nm) from the crystal. The SHG relative efficiency of Piperazine di-orthophosphate crystal was found to be 0.85 times higher than that of KDP.

4. Conclusion

Optical quality single crystals of Piperazine diorthophosphate were grown using solution growth method by slow evaporation of solvent technique. Structural analyses were carried out by single crystal XRD and powder X-ray diffraction analyses. The crystal planes were indexed using powder XRD. It was observed from the morphology studies that (0 1 0) plane is the most prominent plane among the other well developed planes. The presence of functional groups were confirmed by FTIR spectral analyses. From the optical absorbance spectra, it is observed that the title crystal in the present investigation has a fairly wide transparency range and less absorption in the entire visible region. The crystal is thermally stable upto 160.5 ° C. The second harmonic generation intensity of Piperazine di-orthophosphate was found to be 0.85 times higher than that of KDP crystal. The above results clearly shows that the grown Piperazine diorthophosphate single crystal can be used as a potential material for optical applications.

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