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Growth, structural, optical, thermal and mechanical studies on 4-Aminopyridinium monophthalate: A novel nonlinear optical crystal

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ABSTRACT

A novel nonlinear optical crystal of 4-Aminopyridinium monophthalate (4-APMP) was grown by slow evaporation technique using methanol as solvent. Single crystal X-ray diffraction analysis confirms that the grown crystal belongs to orthorhombic system. The presence of functional groups was qualitatively determined by FTIR analysis. The optical absorption studies reveal very low absorption in the entire visible region. The fluorescence emission spectrum shows the emission is in blue region. The thermal stability of the grown crystal is found to be around 197.2 °C. The SHG efficiency of the grown crystal is found to be 1.1 times than that of KDP crystals.

1. Introduction

In recent years, nonlinear optical materials (NLO) have attracted many researchers due to its wide applications in the field of telecommunication, optoelectronic and optical information storage devices [1–8]. Organic NLO materials exhibits much larger NLO efficiencies compared to their inorganic counterpart, thus promises to meet future requirements for ultrahigh bandwidth photonic devices [9–11]. Organic materials have been known for their potential applications in semiconductors, superconductors and nonlinear optical devices [12]. Hence, Organic NLO crystals with high second harmonic generation efficiency and transparency in UV–Vis region are required for numerous device applications. In the present work, single crystals of 4-Aminopyridinium monophthalate have been grown by slow evaporation technique and the grown crystals were subjected to various characterizations such as single crystal XRD, FTIR, UV, Fluorescence, thermal and mechanical analysis and the results were discussed in detail.

2. Experimental details

2.1. Material synthesis

The title compound has been synthesized by dissolving (AR grade) 4-aminopyridine and phthalic acid in methanol in the molar ratio1:1. After continuous stirring, the supersaturated solution was filtered with Whatman filter paper and kept it in the dust free atmosphere. The saturated solution was allowed to dry at room temperature by slow evaporation technique. After the period of 30 days, optically transparent and defect free crystal having dimensions 15 × 3 × 2 mm^3 were grown and the photograph of the grown crystal is shown in the Fig. 1. Moreover, the molecular structure of the 4-aminopyridinium monophthalate single crystal also as shown in Fig. 2. The chemical reaction of the synthesized material is given as follows:

$$C_5H_6N_2 + C_8H_6O_4 \rightarrow C_{13}H_{12}N_2O_4$$

2.2. Characterisation

The grown crystal was subjected to Single crystal X − ray diffraction analysis to resolve the structure using ENRAF NONIUS CAD 4/MACH 3 single crystal X-ray diffractometer. The presence of functional groups was determined qualitatively using

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0022-2860/

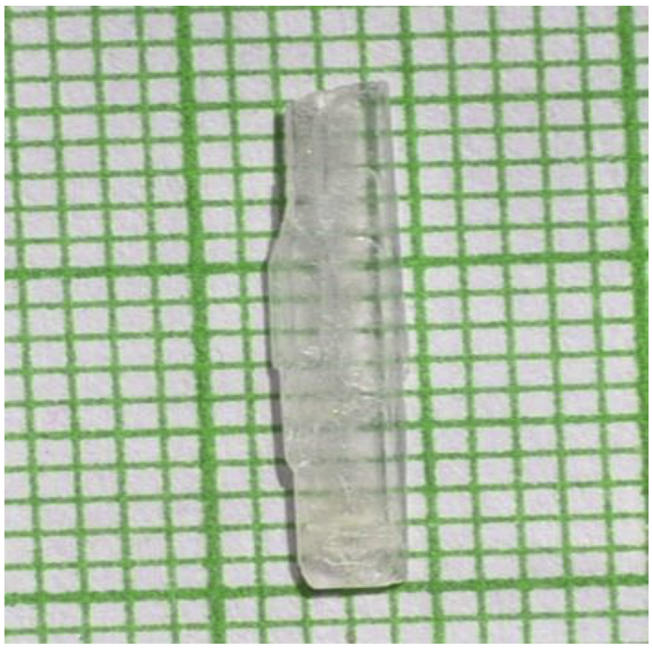

Fig. 1. Photograph of as grown crystal.

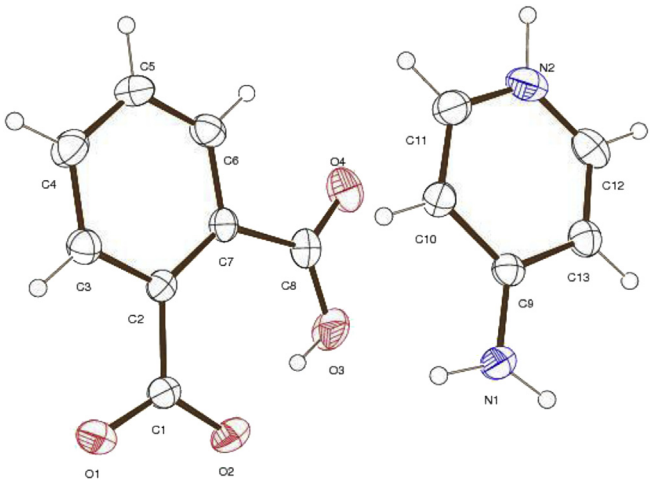

Fig. 2. Molecular structure of 4-APMP crystal.

Perkin–Elmer Paragon-500 spectrometer. Optical studies were carried out using VARIN CARY 5E UV-VIS-NIR spectrophotometer. The thermal stability of the title crystal was carried out by using NETZSCH STA 409C analyzer. The mechanical hardness studies were carried out using Leitz Wetzler Microhardness tester with a diamond pyramidal indenter. The powder SHG efficiency of the grown crystal was studied using Q-switched Nd: YAG laser by employing the Kurtz and Perry powder technique.

3. Results and discussion

3.1. Single crystal X-ray analysis

The grown crystal having dimensions 0.35 × 0.30 × 0.25 mm^3 was subjected to single crystal XRD analysis using Enraf Nonius CAD 4/MACH 3 single crystal X-ray diffractometer using Mo Kα radiation (λ = 0.71073 Å). The crystal structure of the title compound (CCDC No. 1028946) was solved by the direct method using the program SIR-92 (WINGX) [13]. Data were collected in frames using oscillation method with μ ranging between 2.59 and 25.00. Full matrix least-squares refinement was done using SHELXL-97 (WINGX) computer program [14,15]. Tables 1–7 give the details of the crystal and experimental data. Fig. 2 represents the ORTEP (Oak Ridge Thermal Ellipsoid Plot) diagram of the molecule with atom numbering with the unit cell projected down the *b*-axis. There are two molecules of the title compound in the asymmetric unit. The phthalate ion is getting attached to 4-Aminopyridine molecules. Further, the analysis reveal that the title crystal belongs to orthorhombic system with non centrosymmetric space group $P2_12_12_1$ and the lattice parameters are a = 5.340 Å, b = 8.223 Å, c = 27.366 Å, α = β = γ = 90° and V = 1201.66 $Å^3$.

3.2. FTIR spectral study

Fourier transform infrared spectrum (FTIR) of the 4-APMP crystal was recorded in the range of 400–4000 cm^{-1} using Perkin Paragon-500 through KBr pellet technique and is shown in Fig. 3. A broad band at 3350 cm^{-1} is due to NH_2 symmetric stretching. The peaks at 1928 and 955 cm^{-1} is assigned to C–C–C ring breathing. The C–H in plane is found to be at 1157, 1026 and 620 cm^{-1}. The peaks at 833 and 732 cm^{-1} is due to C–H out of plane. All these assignments illustrate the presence of 4-Aminopyridinium monophthalate and the assignments were shown in the Table 8.

3.3. Optical absorption analysis

An optical absorption spectrum of the grown crystal was carried out between from 200 to 1500 nm using VARIN CARY 5E UV-VIS-NIR spectrophotometer and is shown in Fig. 4. The optical studies

Table 1
Crystal data and structure refinement for 4 -APMP.

Identification code	Shelxl
Empirical formula	C13H12 N2 O4
Formula weight	260.25
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P_{212121}
Unit cell dimensions	a = 5.340 [10] Å
	b = 8.223 [2]Å
	c = 27.366 [8] Å
α	90°
β	90°
γ	90°
Volume	1201.66(5) A^3
Z, Calculated density	4, 1.439 Mg/m^3
Absorption coefficient	0.109 mm^{-1}
F (000)	544
Crystal size	0.35 × 0.30 × 0.25 mm^3
Theta range for data collection	2.59–25.00 deg.
Limiting indices	−6 ≤ h<=6, −9 ≤ k<=9, −32 ≤ l<=31
Reflections collected/unique	5415/2122 [R (int) = 0.0187]
Completeness to theta	25.00 99.8%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9865 and 0.9365
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2122/0/185
Goodness-of-fit on F^2	1.064
Final R indices [I > 2sigma (I)]	R1 = 0.0308, wR2 = 0.0740
R indices (all data)	R1 = 0.0354, wR2 = 0.0769
Absolute structure parameter	−0.3(11)
Extinction coefficient	0.0053(15)
Largest diff. peak and hole	0.154 and −0.124 $e.A^{-3}$