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Growth, structure and spectroscopic studies of an organic optical material: 4-Aminopyridinium 4-nitrophenolate 4-nitrophenol single crystal

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Organic nonlinear optical (NLO) crystals play an important role in optical device fabrication. The use of *p*-nitro phenol for the production of crystalline salt with aromatic base is of considerable interest for the nonlinear optical applications. Single crystals of 4-aminopyridinium 4-nitrophenolate 4-nitrophenol (4AP4NP) were grown by the slow evaporation solution growth technique. The obtained crystals were characterized by single crystal X-ray diffraction analysis, FT-IR and FT-Raman spectral studies. The unit cell parameters and space group of 4AP4NP crystal were estimated by single crystal X-ray diffraction analysis. The presence of functional groups and their corresponding vibrations were studied through FT-IR analysis. The chemical components present in the crystal were further confirmed by FT-Raman spectroscopy.

Keywords: Single crystal, solution growth, FT-IR, FT-Raman.

Introduction

Organic nonlinear optical (NLO) crystals play an important role in electro-optic modulators, frequency mixing, second harmonic generation and optical parametric oscillation, etc.[1, 2]. The use of *p*-nitrophenol for the production of crystalline salts with aromatic base, suitable for the single crystal characterization has been employed extensively. In the present work growth, crystal structure and spectral studies have been studied on 4-aminopyridinium 4-nitrophenolate 4-nitrophenol (4AP4NP) crystals.

Experimental

Synthesis and crystal growth:

Commercially available high pure raw materials, 4-aminopyridine (Merck 99.9%) and 4-nitrophenol (Merck 99.6%) were weighed stoichiometrically, dissolved in toluene and then, the clear solution was heated up to 45°C and maintained. The formation of yellow precipitate after an hour confirmed the formation of 4AP4NP material. The obtained precipitate was washed by toluene as a solvent and dried off using hot air oven. The saturated solution was prepared using ethanol and it was filtered in beaker and kept it in a dust free atmosphere. After a period of 20 days, single crystal of 4AP4NP with the dimension of 15×8×5 mm^3 was harvested and is shown in Fig. 1 (a) and (b).

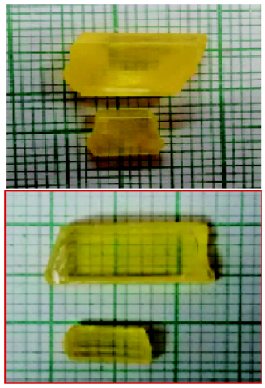

Fig. 1. Photograph of (a) as-grown and (b) cut and polished 4AP4NP crystals.

Results and discussion

Single XRD analysis:

The unit cell parameters of 4AP4NP single crystal were estimated using a Bruker Kappa APEXII single crystal X-ray diffractometer with MoK_{α} (λ = 0.71073 Å) radiation. The cal-

culated cell parameters are a = 5.603 (Å), b = 15.30 (Å), c = 10.779 (Å), β = 102.71° and V = 901 Å^3 and well matched with the reported values[3].

FT-IR spectral analysis:

FT-IR spectra of 4AP4NP sample were recorded on Nicolet Avator 330A spectrophotometer in the range 4000–400 cm^{-1}. Fig. 2 shows the FT-IR spectra of 4AP4NP crystals. The observed frequencies of vibrations their assignments are given in Table 1. The NH^+ rocking is observed in 501 cm^{-1} and COO^- in-plane bending is observed in 643 cm^{-1} which confirms the presence of amine and carboxylic group in the crystalline material.

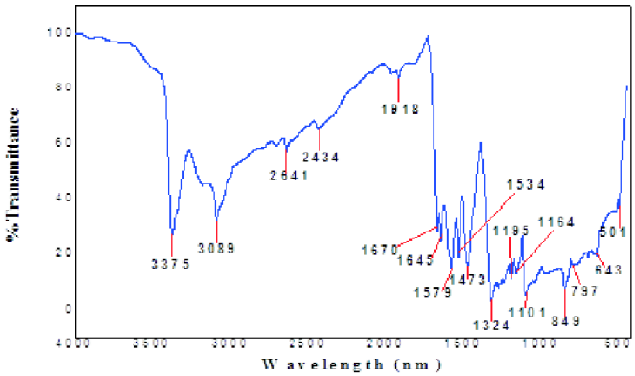

Fig. 2. FT-IR spectra of 4AP4NP crystals.

Table 1. Vibrational frequencies for 4AP4NP crystals

Wavenumber (cm^{-1})		Assignment
FT-IR	FT-Raman	
3375		N-H stretching
3089	3067	N-H stretching
2641, 2434		C-H stretching
1670		Stretching mode of carboxylate anion
1645		C=C stretching
1579, 1534	1595, 1578	C=N stretching
1473	1499	Phenyl stretching
1324	1334, 1306	C-O stretching
1280, 1195, 1101	1242	NO_2 symmetric stretching
1164	1166	O-H in-plane bending
1045	1102, 1046	C-C-N asymmetric stretching
849, 797, 702	863	CH_2 rocking
643	638	COO^- in-plane bendig
501	522	N-H^+ rocking

FT-Raman spectral analysis:

In order to analyze the chemical components present in the crystal was further confirmed by FT-Raman spectroscopy (Fig. 3) and the spectrum was recorded in the range 400–4000 cm^{-1} using BRUKER Laser Raman spectrometer. The observed frequencies of vibrations their assignments are tabulated in Table 1. The peak observed at 522 cm^{-1} and 638 cm^{-1} corresponds to NH^+ rocking and COO^- in-plane bending modes which further confirms the amine and carboxylic group present in the synthesized crystal.

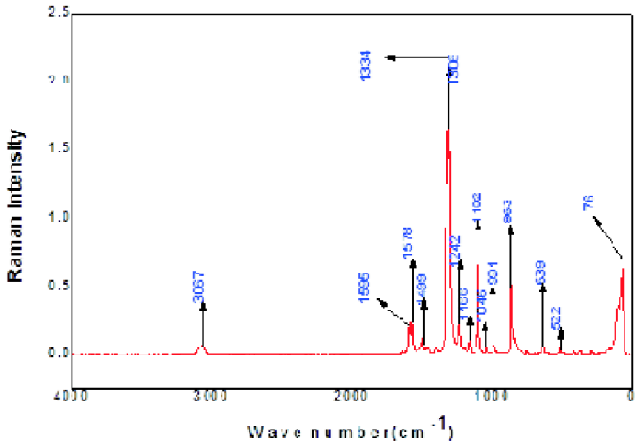

Fig. 3. FT-Raman spectra of 4AP4NP crystals.

Conclusions

Good quality 4AP4NP crystals have been grown by solution growth technique. Crystal structure, functional group and chemical components of the samples were confirmed and analyzed through single XRD, FT-IR and FT-Raman studies.

Acknowledgements

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