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SYNTHESIS, GROWTH, SPECTRAL AND OPTICAL PROPERTIES OF 2-AMINOPYRIDINIUM p-AMINOBENZOATE NONLINEAR OPTICAL SINGLE CRYSTAL

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Abstract: *Organic nonlinear optical crystal of 2-aminopyridinium p-Aminobenzoate have been grown by slow evaporation solution growth method at room temperature using ethanol:water as mixed solvent. From the single crystal X-ray diffraction study, it is confirmed that PA2A crystal belongs to orthorhombic crystal system with space group P. From the powder XRD pattern, the various planes of reflections and crystal perfections were identified. The presence of functional groups in the synthesized compound was identified by FTIR spectral analysis. The cut-off wavelength and transmittance were determined by UV-Visible spectra. From the Photoluminescence spectra, high intensity violet emission peak observed at 360 nm with excited at 345 nm. The Kurtz-Perry powder second harmonic generation technique confirms the nonlinear optical property of the grown crystal. The SHG relative efficiency of PA2A crystal has been found 2.2 times higher than that of KDP.*

Keywords: *Organic, NLO, crystal growth, structural, spectral and optical properties*

I. INTRODUCTION

The organic materials with aromatic ring which are of greatly interested for the second and third-order non linear optical applications due to their high non linearity and high optical damage threshold and their ultra fast, almost purely electronic response [1-3]. The large nonlinear optical coefficients, quick response time, more opportunity of manipulations during the synthesis to obtain the desired structure and the cost effects are the special features of organic materials [4]. In addition to, this organic crystalline materials exhibit large nonlinear response compared to inorganic and also possess high thermal stability, high packing densities and larger photochemical stabilities due to the presence of intermolecular hydrogen bonding between counter ions. These H-Bonding formed by the interaction of an electron donor and electron acceptor groups present in the molecular system [5,6]. Organic ionic crystals with hetero aromatic electron acceptor pyridinium, imidazolium and quinolinium possess a strong electron withdrawing characteristics large second order nonlinear response. 2-Aminopyridine, a hetero cylic molecule, with two nitrogen atoms may also be used as a model compound for understanding nucleic acid bases [7]. 4-Aminobenzoic acid (4-ABA) is one of the well known carboxylic acids to promoting molecular self assembly by means of strong hydrogen bonding through its carboxylic acid group [8-9]. In the present investigation, we have synthesized 2-Aminopyridine p-Aminobenzoic acid by slow evaporation method. The grown crystal were characterized by single and powder X-ray diffraction (XRD) analyses, FTIR, UV-VIS Spectroscopy, Photoluminescence, Second order nonlinearity was found by Kurtz-perry.

II. EXPERIMENTAL TECHNIQUES

A. Synthesis and Crystal Growth

2-aminopyridinium p-Aminobenzoate (PA2A) single crystal was grown by using the slow evaporation solution growth method. PA2A crystal was synthesized by taking 2-Aminopyridine and p-Aminobenzoic acid in equimolar ratio and dissolved in 80 ml of ethanol:water mixed solvent. The solution was stirred continuously about 6 h to ensure homogeneous concentration of the solution. The resultant solution was filtered by whatmann filter paper and perforated by polythene sheet to restrict the fast evaporation of the solvent. The solution was allowed for slow evaporation. After the evaporation period of two to three weeks, the spontaneous nucleation was occurred in the supersaturated solution and the developed good quality single crystals were collected. Fig.1 and 2 shows the structure scheme and photograph of the grown crystal respectively.

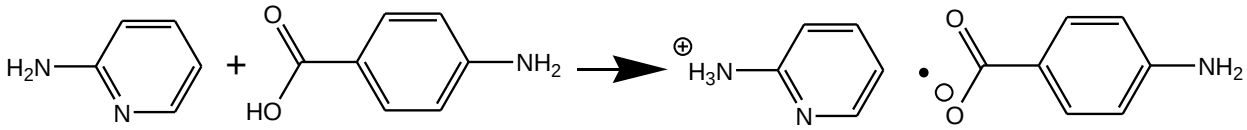

Figure 1. Structure scheme of 2-aminopyridinium p-Aminobenzoate (PA2A)

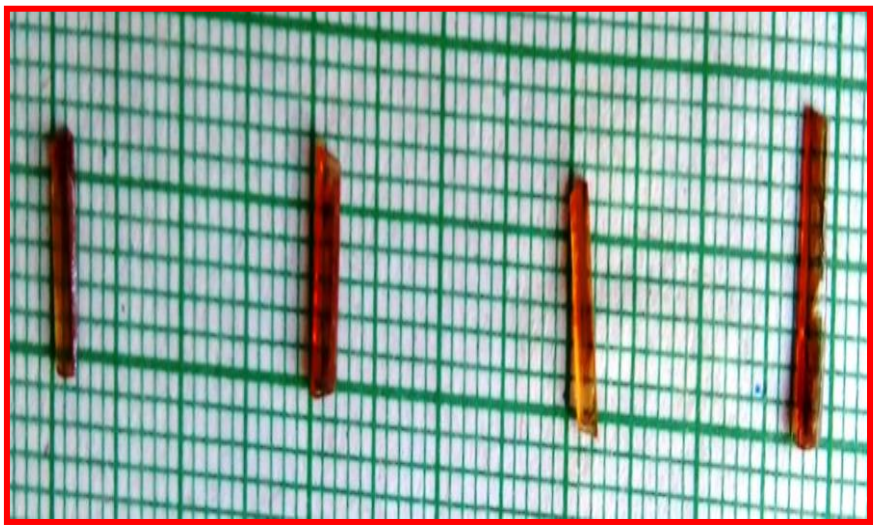

Figure 2. Photograph of the grown crystal of 2-aminopyridinium p-aminobenzoate (PA2A)

III. RESULTS AND DISCUSSION

A. Structural Analyses

The crystalline nature of the grown crystal was carried by powder X-ray diffraction pattern of PA2A crystal using a X'Pert PRO diffractometer with cukα (**λ**=1.5406) radiation. The sample was scanned in the range of 10-80° at the rate of 2°/min. The presence of sharp and well defined peak confirms the good crystalline nature of the PA2A crystal. Single Crystal XRD data of the grown crystal of p-Aminobenzoate 2-Aminopyridinium was obtained by using Brukker kappa APEXII single crystal X-ray Diffractometer with Mokα (**λ**=0.71073). From the single crystal analysis, it was observed that the grown crystal belongs to orthorhombic crystal system with non-centrosymmetric space group P. This type of non-centrosymmetric space group present in the grown PA2A crystal should supports good second order nonlinear property is one of the main criteria for the material to exhibit second harmonic generation property [12]. The estimated lattice parameters are a=5.77, b=10.52, c=19.27, α=90.00°, β=90.00°, γ=90.00°, V=1170 Å^3.

Table 1. Structural Parameters of PA2A crystal

Crystal data	**PA2A**
Empirical formula	$C_5H_7N_2^+ \bullet C_7H_6NO_2^-$
Crystal System	Orthorhombic
Space group	P
Unit cell dimension	a =5.77Å, b=10.52Å, c=19.27Å α=90.00° β=90.00° γ=90.00°
Volume	V=1170Å^3
Temperature(K)	295

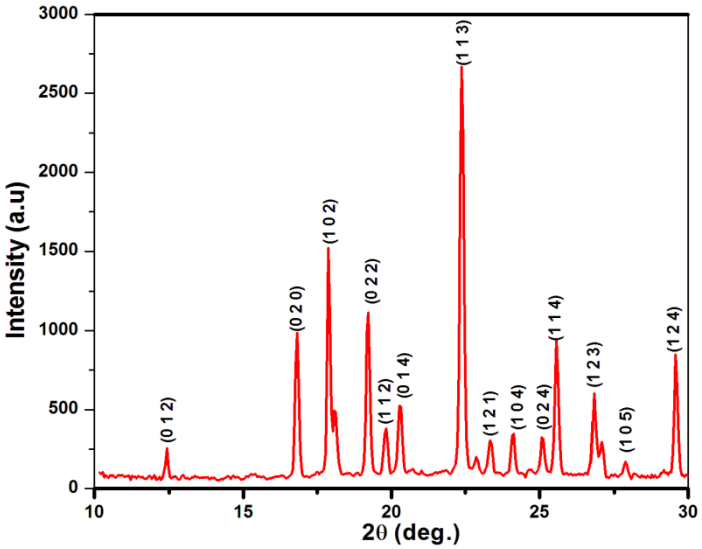

Figure 3. Powder XRD pattern of the PA2A crystal

B. FT-IR:

The FTIR spectral analysis is the important study to understand the various functional groups and structure of a compound. The infrared spectrum was recorded using JASCO FTIR 410 spectroscopy in the wavelength range 400-4000 cm^{-1} by KBr pellet technique. The various types of vibrations and their band assignments were given in table 2. According to Bellamy, vibration bands in the region of 3000-3500 cm^{-1} are usually due to the N-H vibrations. In the present investigation the grown crystal was absorption peak observed at 3342 cm^{-1} is assigned to N-H vibration. The band that appears at 2745 cm^{-1} is due to the presence of O-H Stretching in PA2A Crystal. The weak absorption peak at 2960 cm^{-1} was due to C-H stretching vibration. The peak observed at 1080 cm^{-1} belongs to C-N Stretching. C-O stretching vibration appears as a strong band in the region 1300-1200 cm^{-1}. In this present case the corresponding C-O stretching vibration peak observed at 1283 cm^{-1} in FTIR spectrum. The C=C stretching vibration of the aromatic ring falls at 1430 cm^{-1} in FTIR spectrum. The aromatic C-C Stretching vibrations occurred in the region 1500-1400 cm^{-1}. In The present investigation C-C stretching vibration peak observed at 1492 cm^{-1}.

Table 2. Vibrational Assignments of PA2A crystal

Wavenumber cm^{-1}	**Assignments**
3342	N-H Stretching secondary amine
2745	O-H stretching
2960	C-H Stretching
1080	C-N Stretching
1430	C=C Stretching
1492	C-C Stretching
1283	C-O Stretching
1675	C=O Stretching

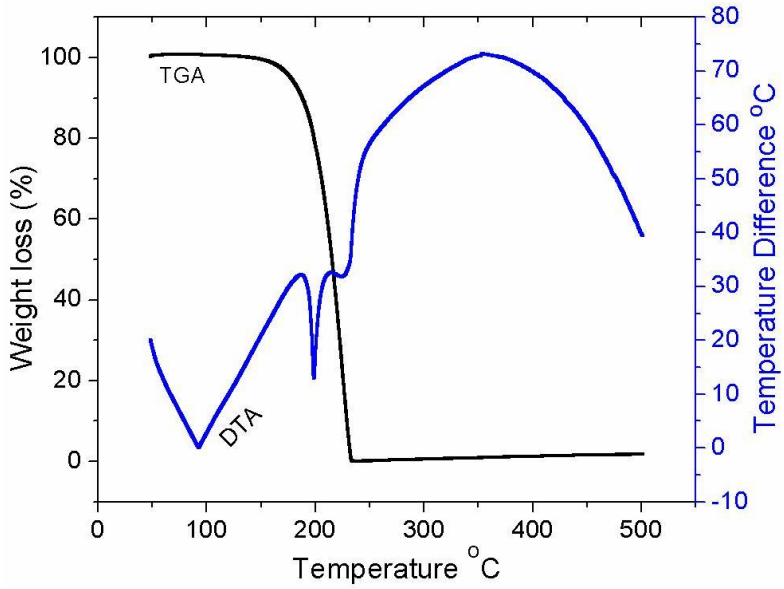

Figure 4. FTIR spectrum of PA2A crystal

C. UV-Vis Studies

The UV-Vis Spectrum gives information about the structure of the molecule because it involves the promotion of the electron in σ and Π orbital from the ground state to the higher energy states by absorbtion of UV light. UV-Visible spectrum of PA2A crystal was recorded using UV-Vis Spectrometer in the range between 250 nm to 900 nm. The cutoff wavelength is very important property for an NLO crystal. The lower cutoff found to be 315 nm which combined with good transparency attests to the usefulness of PA2A crystal for opto-electronic devices.

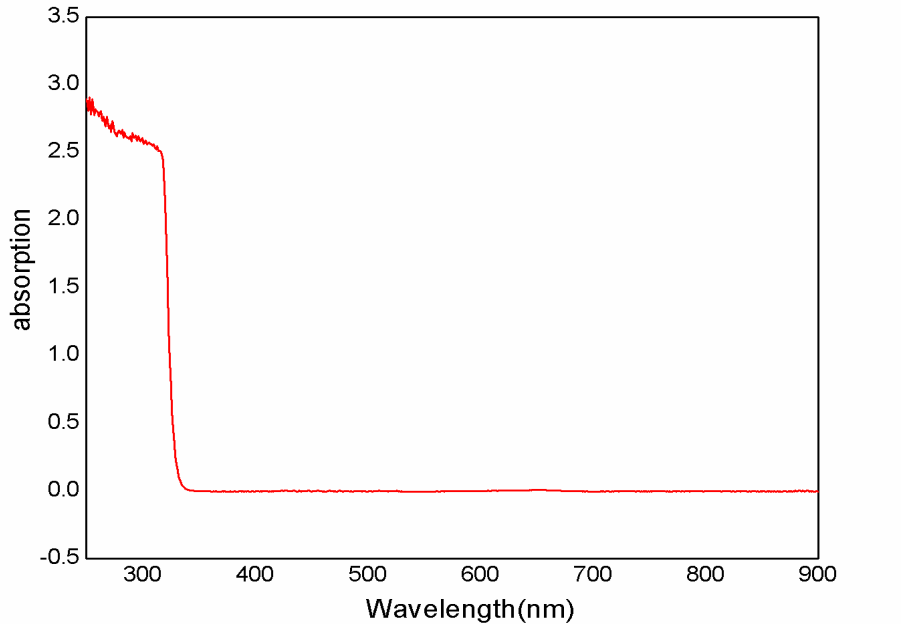

Figure 5. UV-Vis Absorbtion spectrum of PA2A crystal

Determination of Optical band gap(Eg)

The optical band gap of the grown PA2A crystal, the absorbsance spectrum was recorded at room temperature. The absorption coefficient was calculated from the absorbsance spectrum based on the following relations,

Where is the T is the transmittance and d is the thickness of the sample

$$\alpha = (1/d)\log(1/T)$$

$$h\nu\alpha = A(h\nu - E_g)^{1/2}$$

Where A is a constant h is planck's constant, ν is frequency of the incident radiation and Eg is the optical energy bandgap. The bandgap energy value (Eg) was obtained by extrapolating the linear portion of the plot to intercept the photon energy axis and value was found to be 3.7 eV. As a consequence of wide band gap, the grown crystal has a large transmittance in the visible region.

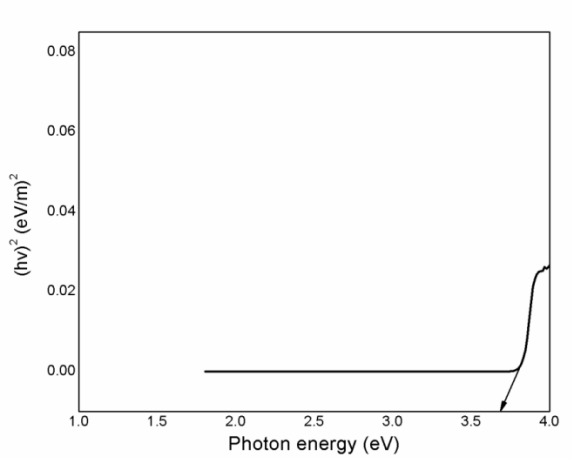

Figure 6. Band gap Energy of PA2A crystal

D. Photoluminescense studies

Luminescent materials are substances which convert incident energy input into the emission of electromagnetic waves in the ultraviolet, visible or infrared regions and above that due to black body emission. Photoluminescense (PL), where the luminescence is stimulated by UV or Visible light, is a widely used technique to identify the impurities and finds applications in lightning technologies. In particular, PL is a fundamental tool to determine a class of energy levels that are invisible at Uv-Vis absorption measurements. The emission spectra of PA2A crystal was recorded in the range of 250-480 nm, the excitation wavelength of PA2A crystal was 345 nm and the emission peak was observed at 360 and 385 nm. A sharp peak was obtained which confirmed the emission of violet light from the material.

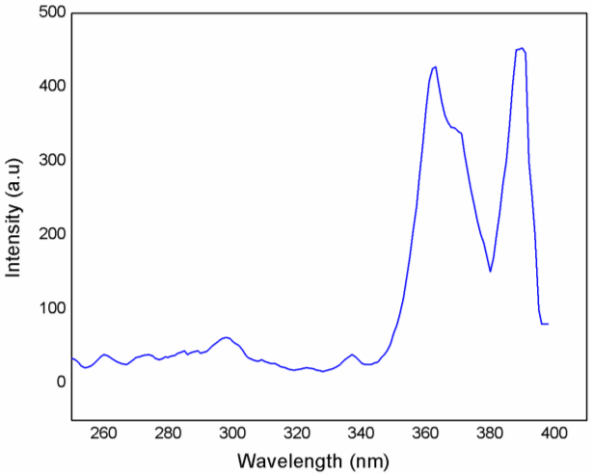

Figure 7. PL Spectra of PA2A crystal

E. Non-linear optical test

The SHG property in PA2A crystal was studied using a Q-switched Nd: YAG laser by employing Kurtz powder test with KDP as a reference. The fundamental beam of an Nd:YAG laser with 1064 nm wavelength is focused on to the powdered sample. It is important to evaluate the efficiency of NLO materials. The SHG signal generated in the sample was confirmed by the emission of green radiation (532 nm) from the sample and the optical signal was collected by a photomultiplier tube. The optical signal incident on PMT was converted into a voltage output at the CRO. The SHG Efficiency of PA2A crystal is found to be 2.2 times greater than that of KDP.

IV. CONCLUSION

The bulk size single crystals of PA2A were grown by slow evaporation solution growth technique. From the single crystal X-ray diffraction study, the grown crystal belongs to orthorhombic structure with non centrosymmetric

spacegroup p, the cell parameters were estimated, which and shows good crystalline nature. The modes of vibration of the functional groups were identified using FT-IR spectra. The grown crystal possess good optical transparency in the wavelength range of 200-1000 nm with UV cutoff wavelength at 315 nm and the optical energy bandgap was determined to be 3.7 eV from UV-Vis Spectral studies. The excitation wavelength of PA2A crystal was 345 nm and the emission peak was observed at 360 and 385 nm. The SHG relative efficiency of PA2A crystal was found to be 2.2 times that of KDP.

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