CHAPTER 5

GROWTH AND CHARACTERIZATION OF 2-AMINO-4-PICOLINIUM 4-AMINOBENZOATE SINGLE CRYSTALS

5.1 INTRODUCTION

Organic compounds containing push-pull conjugation can present large optical second-order molecular polarizabilities and have important applications in second-order nonlinear optical (NLO) devices. Depolarization and intermolecular charge transfer effect of $\pi$ electrons in these molecules can cause large and fast nonlinear responses (Chemla and Zyss 1987). In addition to the well established inorganic crystals such as potassium dihydrogen phosphate ($\text{KH}_2\text{PO}_4$), Lithium Niobate (LiNbO$_3$); Potassium titanyl phosphate (KTiPO$_4$) and Barium borate ($\beta\text{-BaB}_2\text{O}_4$); 3-methyl-4-nitropyridine-1-oxide (POM) (Zyss et al 1981) and N-4-Nitrophenyl-L-Prolinol (NPP) (Zyss et al 1984) have emerged as extremely efficient new inorganic and organic NLO materials. In the above said organic crystals, two requirements are satisfied.

(i) They are made of highly polarizable molecules, the so called conjugated molecules, where highly delocalized $\pi$-electrons can easily move between electron donor and electron acceptor groups on opposite sides of the molecule, including a molecular charge transfer.
(ii) The molecules are adequately packed to build up a noncentro symmetrical crystal structure that provides nonvanishing second-order nonlinear coefficients (Chemla and Zyss 1987, Bosshard et al 1995).

This chapter presents the growth of 2-Amino-4-Picoline 4-aminobenzoate (APAB) single crystals by the low temperature solution growth method. 2-Amino 4-Picoline is known as 2-amino 4-methylpyridine. The crystal structure of APAB was reported by Hong Shen et al (2008). The nonlinear optical properties of the title crystal are reported.

The title compound consists of 2-Amino 4-methyl pyridinium cations and 4-amino-benzoate anions. The smaller difference in C-O bond distances of the carbonyl group indicates the carboxyl group is deprotonated in the crystal. The aminobenzoate anions are linked with both of adjacent aminobenzoate anions and amino methylpyridinium cations via N-H…O hydrogen bonding to form three dimensional supramolecular structures. The crystal structure (Figure 5.1) contains weak C-H…O hydrogen bonding between adjacent anions. The reactions between 2-Amino 4-methyl pyridine and 4-aminobenzoic acid yields 2-amino 4-methylpyridinium 4-aminobenzoate (Hong Shen et al 2008).
5.2 CRYSTAL GROWTH OF 2-AMINO-4-PICOLINE 4-AMINOBENZOIC ACID (APAB) SINGLE CRYSTALS

The reaction scheme of 2-Amino-4-Picoline 4-aminobenzoic acid (APAB) is shown in Figure 5.2. For the growth of 2-Amino-4-picolinium 4-aminobenzoate (APAB) crystals equimolar ratio of 2-Amino-4-methyl pyridine (Alfa Aesar) and 4-Aminobenzoic acid (Merck-extra pure) were dissolved separately in ethanol at room temperature.
Then the solutions were mixed together and stirred for six hours. Prepared solutions were filtered with Whatman grade No.1 and taken in clean vessels. The vessels were closed with perforated polythene covers and placed in dust free atmosphere. The nucleation was observed in the solution in 7 days and brown crystals of appreciable size were obtained after four weeks. The grown crystals are shown in Figure 5.3.

![Figure 5.3 As grown single crystals of APAB](image)

### 5.3 CHARACTERIZATION OF APAB CRYSTALS

The grown APAB single crystal was confirmed by powder and single crystal X-ray diffraction, using XPERT-PRO diffractometer and ENRAF NONIUS CAD4 diffractometer, respectively. The vibrational frequencies were identified by FT-IR spectral studies using JESCO 416 PLUS FT-IR spectrometer in the range of 4000 cm\(^{-1}\) to 400 cm\(^{-1}\). The microhardness studies were carried out on grown crystal using Vicker’s microhardness tester attached with optical microscope (Leitz Wetzler hardness tester). The grown crystals were subjected to second harmonic generation studies by Nd:YAG laser and green output was obtained. The dielectric behavior was also studied.
5.3.1 Single crystal and Powder X-ray diffraction analyses of APAB

The single crystal XRD data of the grown 2-Amino 4-picolinium 4-aminobenzoate (APAB) crystals were obtained from a single crystal X-ray diffractometer (Model: ENRAF NONIUS CAD4/MACH3) with MoK$_\alpha$ ($\lambda = 0.71073\text{Å}$) and the obtained crystallographic data are given in Table 5.1. From the single crystal XRD analysis it is confirmed that the grown APAB crystallizes in the orthorhombic system with space group P2$_1$2$_1$2$_1$. The powdered sample of APAB single crystal was subjected to powder X-ray diffraction studies with XPERT-PRO diffractometer using CuK$_\alpha$ radiation of wavelength 1.54060 Å. The peaks observed from X-ray diffraction spectrum were indexed using the Proszki software package. The powder X-ray diffraction pattern of APAB is shown in Figure 5.4.

Table 5.1 Crystallographic data of APAB

<table>
<thead>
<tr>
<th>Lattice Parameters</th>
<th>Present work</th>
<th>Reported value (Hong Shen et al 2008)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>5.585(1)Å</td>
<td>5.5734(14)Å</td>
</tr>
<tr>
<td>b</td>
<td>8.801(4)Å</td>
<td>8.8154(16)Å</td>
</tr>
<tr>
<td>c</td>
<td>25.294(1)Å</td>
<td>25.374(5)Å</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>90°</td>
<td>90°</td>
</tr>
<tr>
<td>$\beta$</td>
<td>90°</td>
<td>90°</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>90°</td>
<td>90°</td>
</tr>
<tr>
<td>Volume</td>
<td>1243.3(9)Å$^3$</td>
<td>1246.6(5)Å$^3$</td>
</tr>
</tbody>
</table>
5.3.2 High Resolution X-ray diffraction (HRXRD) studies of APAB

Figure 5.5 shows the high-resolution diffraction curve (DC) recorded for a APAB single crystal specimen grown by slow evaporation solution growth technique (SEST) using (011) diffracting planes in symmetrical Bragg geometry by employing the multicrystal X-ray diffractometer with MoKα₁ radiation. As seen in the Figure 5.5, the DC contains a single peak and indicates that the specimen is free from structural boundaries. However, it is quite broad with full width at half maximum (FWHM) of 105 arc s which is quite higher than that expected from the plane wave theory of dynamical X-ray diffraction (Batterman and Cole 1964) for an ideally perfect crystal. This much broadness with good scattered intensity along the wing of the DC indicates that the crystal contains point defects and their aggregates. More details may be obtained from the study of
high-resolution diffuse X-ray scattering measurements (Lal and Bhagavannarayana 1989), which is not the main focus of the present investigation. The small kinks at the top of the curve indicate that the crystal contains mosaic blocks which are mis-oriented to each other by few seconds to few minutes of arc.

Figure 5.5 High-resolution X-ray diffraction curve

5.3.3 Spectral properties
  5.3.3.1 Factor group analysis

The factor group method provides a basis for the prediction of theoretical lattice vibrations which can be obtained by IR and Raman spectral analyses. The single crystal X-ray diffraction analysis carried out for C₆H₉N₂⁺.C₇H₆NO₂⁻ confirms the grown crystal belongs to orthorhombic crystal system with space group P2₁2₁2₁ (Dᵥ̄). The factor group analysis for APAB crystal was carried out by following the procedures outlined by Rousseau et al (1981). There are totally four atoms per unit cell, which
occupies the general sites of $C_1 (4)$ symmetry. There are 33 atoms in a single molecule of the title compound, which in turn gives rise to $(33 \times 4) = 132$. Group theoretical analysis of the fundamental modes of APAB crystal predicts that there are 396 vibrational optical modes and are seen to decompose into $\Gamma_{396} = 99A + 98B_1 + 98B_2 + 98B_3$ apart from three acoustic modes $B_1 + B_2 + B_3$. The summary of the factor group analysis of 2-Amino 4-picobilinum 4-aminobenzoate (APAB) is given in Table 5.2.

**Table 5.2 Factor group analysis - Summary of APAB**

<table>
<thead>
<tr>
<th>Factor Group Symmetry</th>
<th>Site Symmetry</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>O</th>
<th>Optical Mode</th>
<th>Acoustical Mode</th>
<th>Total</th>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ext</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>IR</td>
</tr>
<tr>
<td>A</td>
<td></td>
<td>93</td>
<td>45</td>
<td>9</td>
<td>6</td>
<td>99</td>
<td>0</td>
<td>99</td>
<td>$\alpha_{xx}, \alpha_{yy}, \alpha_{zz}$</td>
</tr>
<tr>
<td>B_1</td>
<td>3T,4R</td>
<td>93</td>
<td>45</td>
<td>9</td>
<td>6</td>
<td>99</td>
<td>1</td>
<td>98</td>
<td>Z</td>
</tr>
<tr>
<td>B_2</td>
<td>3T,4R</td>
<td>93</td>
<td>45</td>
<td>9</td>
<td>6</td>
<td>99</td>
<td>1</td>
<td>98</td>
<td>Y</td>
</tr>
<tr>
<td>B_3</td>
<td>3T,4R</td>
<td>93</td>
<td>45</td>
<td>9</td>
<td>6</td>
<td>99</td>
<td>1</td>
<td>98</td>
<td>X</td>
</tr>
<tr>
<td>Total</td>
<td>9T,12R</td>
<td>372</td>
<td>156</td>
<td>180</td>
<td>36</td>
<td>24</td>
<td>3</td>
<td>393</td>
<td></td>
</tr>
</tbody>
</table>

**5.3.3.1.1 Vibrational analysis of APAB**

The vibrational analysis of APAB reveals the structure of the coordinated compounds, information on the nature of bonding and the confirmation of the material. The predicted modes of vibrations of APAB could be due to lattice vibrations and internal vibrations of the coordinated compounds mostly the C-H, N-H and O-H groups. The fundamental modes of vibrations of APAB obtained from the theoretical calculation reveal 372 internal vibrations and 24 external modes. The external modes are classified
into 9 translational and 12 rotational modes apart from 3 acoustic modes. The bands observed between 4000 cm\(^{-1}\) and 400 cm\(^{-1}\) are due to the internal vibrations of the coordinated compounds. The components \(A (\alpha_{xx}, \alpha_{yy}, \alpha_{zz})\), \(B_1(\alpha_{xy})\), \(B_2(\alpha_{xz})\) and \(B_3(\alpha_{yz})\) are Raman active and \(B_1(zz), B_2(yy)\) and \(B_3(xx)\) are IR active (Fateley et al.1972) are given in Table 5.3.

**Table 5.3 Correlation scheme of APAB**

<table>
<thead>
<tr>
<th>Site Symmetry</th>
<th>Factor group Symmetry</th>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A^{393})</td>
<td>99A</td>
<td>(\alpha_{xx}, \alpha_{yy}, \alpha_{zz})</td>
</tr>
<tr>
<td></td>
<td>98B(_1)</td>
<td>(Z)</td>
</tr>
<tr>
<td></td>
<td>98B(_2)</td>
<td>(Y)</td>
</tr>
<tr>
<td></td>
<td>98B(_3)</td>
<td>(X)</td>
</tr>
</tbody>
</table>

5.3.3.1.2 Internal modes

The internal vibrations are those arising from the C-H, C=N and O-H bonding modes of vibrations.

(i) C-H bonding

In APAB crystal the molecules are associated with each other due to molecular dipole moment, which contributes susceptibility to hold the molecules together in crystals. Hetroaromatics such as pyridine shows C-H stretching vibrations at 3044 cm\(^{-1}\).
(ii) C=N bonding

The C=N vibrations of APAB crystal exhibit the absorption band at 1553 cm\(^{-1}\).

(iii) Hydrogen bonding

The broad band observed in the region between 3044 cm\(^{-1}\) to 2644 cm\(^{-1}\) is due to the stretching modes of OH group. The presence of OH group arises from strong hydrogen bonding indicates the enhancement of nonlinear optical property in the title compound (Silverstein 2005).

5.3.3.1.3 External modes

The external vibrations are mainly due to the bands observed below 400 cm\(^{-1}\), owing to the rotational and translational modes of vibrations of ions of APAB crystal. The rotational modes are expected to have higher frequency and intensity than translational modes in the Raman spectra (Bhatacharjee 1990, Hanuja and Fomitsev 1980). APAB is found to have 24 external modes and these vibrations can be achieved experimentally by polarized Raman measurements.

5.3.4 Fourier Transform Infrared (FT-IR) spectral analysis

The FT-IR spectrum was recorded using JESCO 416 PLUS FT-IR spectrophotometer (KBr pellet technique) in the range 4000 cm\(^{-1}\) – 400 cm\(^{-1}\). The recorded FT-IR spectrum of APAB is shown in Figure 5.6. Heteroaromatics such as pyridine shows C-H stretching vibration at 3044 cm\(^{-1}\) and C = C stretching absorptions in the region between 1642 cm\(^{-1}\) and 1614 cm\(^{-1}\). The C = N stretching modes are assigned to peak at 1553 cm\(^{-1}\).
The asymmetric ($\nu_{\text{asym}}$) and symmetric ($\nu_{\text{sym}}$) stretching bands of the N-H group in the 4-aminobenzoic acid are assigned at 3474 cm$^{-1}$ and 3325 cm$^{-1}$, respectively. The very broad band in the region of 3044 cm$^{-1}$ – 2645 cm$^{-1}$ is assigned to the stretching modes of OH group which arises from the strong hydrogen bonding (Chtioui et al. 2005, Samsonowicz et al. 2005).

![Figure 5.6 FT-IR Spectrum of APAB](image)

**Figure 5.6 FT-IR Spectrum of APAB**

### 5.4 MELTING POINT AND DENSITY MEASUREMENTS

The melting point of APAB was noted as 170.3°C (accuracy ±1°C) from the melting point apparatus.
The density of the grown material was found by floatation technique (Mythili et al 2007a). The experimentally determined value is in good agreement with the theoretically found value using the formula given below.

\[
\rho = \frac{(MZ)}{(NV)} \tag{5.1}
\]

where \( M \) is the molecular weight, \( Z \) is the number of molecules per unit cell, \( N \) is the Avogadro’s number and \( V \) is the volume of the unit cell (Wenwei Ge et al 2005). The theoretical value is obtained from the crystallographic data. The obtained density values both by experiment and theoretical are given below.

- Experimental: 1.305 g/cm\(^3\)
- Theoretical: 1.306 g/cm\(^3\)

### 5.5 Optical Studies of APAB Crystal

The optical absorption spectrum of APAB crystal was recorded in the wavelength range from 200 nm to 800 nm covering entire ultraviolet and visible region using UV-Vis. Spectrophotometer (PERKIN ELMER LAMDA 35) with an optically polished APAB single crystal with a thickness of 2 mm. The region from 200-400 nm is important, which provides the large transparent window regarding NLO characteristics. An electron under impact by an incident photon is excited to an intermediate state where it interacts with lattice vibrations and it reaches a final state, the net result being the absorption of photons (Mersch et al 1993).
Figure 5.7 UV-Vis. spectrum of APAB crystal

The plot between transmittance and wavelength for APAB crystal is shown in Figure 5.7. This graph shows the absence of absorbance due to electronic transitions in APAB crystal. This also rules out the possibility of any overtones or combination modes above the threshold values of wavelength. The absorbance in the visible region is an important requirement for the NLO applications. The cutoff wavelength of the APAB crystal is 366 nm. The transmittance window of APAB crystal in the range 366 nm–800 nm is sufficient for the generation of second harmonic light (532 nm) from Nd:YAG laser (1064 nm).
5.6 DIELECTRIC STUDIES

Dielectric properties are correlated with the electro-optic property of the crystal (Benet and Gnanam 1994). Carefully discerned samples of APAB were cut and polished on a soft tissue paper with fine grade alumina powder dispersed in a mixture of acetone and water (1:1). Each sample was electroded on both sides with silver paste (air-drying) to make the sample behaves as a parallel plate capacitor. The sample thickness was 2.24 mm. A HIKOI 3635 model LCR meter was used to measure the capacitance, dielectric loss and resistance of the sample as a function of frequency. A small cylindrical furnace (20 cm × 20 cm × 20 cm), controlled by a Eurotherm temperature controller (± 0.01°C) was used to house the sample. The dielectric constant was calculated by using the relation given in equation 2.1.

The Figure 5.8 shows the variation of dielectric constant with frequency at 35°C, 50°C and 100°C. It is clear from Figure 5.8 that dielectric constant of 2-Amino 4-picolinium 4-aminobenzoate (APAB) crystal decreases gradually with increasing frequency. This is normal dielectric behaviour. The electronic, ionic or atomic, dipolar or orientation and space charge or interfacial polarization are predominant at low frequencies. On increasing frequency the contributions of different polarization decrease. At very high frequencies ($10^{15}$ Hz), only electronic polarization contributes to dielectric constant, while ionic polarization takes place at IR frequencies ($\sim10^{13}$ Hz) (Basharat Want et al 2007).
Figure 5.8 Variation of dielectric constant with frequency of APAB crystal

The change in dielectric loss ($\tan\delta$) with frequency is shown in Figure 5.9. It is observed that the dielectric loss decreases with increasing frequency. The low value of dielectric loss indicates good quality of the crystal. This characteristic property of low dielectric loss with high frequency supports the enhanced optical quality with lesser defects and this property is of vital importance for NLO applications (Varma et al. 1983). The larger value of dielectric constant and dielectric loss ($\tan\delta$) at lower frequencies may be attributed to space charge polarization owing to charged lattice defects (Smyth 1965).
5.7 THERMAL ANALYSIS

The thermogravimetric spectrum was recorded for 2-Amino 4-picolinium 4-aminobenzoate (APAB) crystals in the nitrogen atmosphere between 50 and 500°C using NETZSCH STA 409 C/CD TGA unit. The recorded thermogravimetric spectrum of APAB is shown in Figure 5.10. There is no weight loss between 50°C and 170°C, which indicates that there is no inclusion of solvent in the crystal lattice. The thermogram spectrum reveals that the major weight loss (around 97%) starts at 170.1°C and it continues up to 250°C. The nature of weight loss indicates the decomposition point of the material. However, below this temperature no weight loss is observed. In the DTA spectrum an irreversible exothermic peak observed around 170.1°C corresponds to the decomposition temperature of the material.
5.8 SECOND HARMONIC GENERATION (SHG) TEST

The Second Harmonic Generation (SHG) was tested using Kurtz and Perry powder technique (1968). A fundamental laser beam of 1064 nm wavelength (Nd:YAG laser) with the energy of 1.45 mJ/pulse was used for SHG analysis. KDP and Urea crystals were powdered separately to the identical size and were used as reference materials in the SHG experiment for comparison. The SHG output of APAB was found to be 355 mV and 95 mV for KDP and 525 mV for urea.

5.9 MICROHARDNESS TEST

As grown 2-Amino 4-picolinium 4-aminobenzoate crystals were subjected to static indentation tests at room temperature using a vicker’s microhardness tester equipped with a diamond pyramid intender attached to
an incident light microscope. Indentations were made on the samples with the loads ranging from 5 g to 80 g and the indentation time was kept constant as 3s. Five indentations were made on surface under examination for the same load. Both the diagonals of each impression were measured and an average of 10 diagonal lengths for each load was taken for calculations. To avoid surface effects, the distance between any consecutive indentations was kept more than five times the diagonal length of the indentation mark. The diagonal length of the indentation marks was measured using a filar micrometer eyepiece at a magnification 200X. The Vicker’s hardness ($H_v$) values at different loads were calculated using the expression given in equation 2.2.

### 5.9.1 Load dependence of Hardness

In the present study the indentation marks were made on APAB single crystals. Figure 5.11 shows the plot between hardness number and load which indicates the hardness value increases with increasing load. This is known as load dependent hardness. The observed increase in hardness with increasing load is usually termed as reverse indentation size effect (ISE). In the case of the reverse ISE a specimen does not offer resistance or undergo elastic recovery, but undergoes relaxation involving a release of the indentation stress away from the indentation site. This leads to a larger indentation size which gives rise to a lower hardness at low loads. The indented surfaces of APAB crystals exhibit the formation of cracks at around 80 g. Such cracks are typical for brittle materials. A plot (Figure 5.12) obtained between log (P) and log (d) gives more or less a straight line.
Figure 5.11  Plot between load and hardness number

Figure 5.12  Plot between log P and log d
5.10 CONCLUSION

A novel second harmonic NLO material of APAB has been successfully grown by solution growth technique. From the molecular structure of APAB, it is inferred that the main component of the crystal to provide enhanced NLO efficiency is due to 2-Amino 4-picoline. The optical transparency window will hold good for blue laser generation. The theoretical factor group analysis of APAB predicts 396 total vibrational optical modes that decompose into \( \Gamma_{\text{total}} = 99A + 98B_1 + 98B_2 + 98B_3 \) apart from three acoustic modes. The SHG output is found to be 355 mV and for urea it is 525 mV. The variation of dielectric constant of APAB as a function of frequency suggests that the dielectric constant is relatively higher in low frequency region and lower in high frequency region which substantiate that this material is a promising one for NLO applications.