CHAPTER 5
SYNTHESIS, GROWTH AND CHARACTERIZATION OF NONLINEAR OPTICAL BIS(2-AMINOPYRIDINIUM) SULFATE SINGLE CRYSTALS

5.1 INTRODUCTION

New types of hybrid nonlinear optical materials have been explored from organic-inorganic complexes with stronger ionic bond. L-arginine phosphate monohydrate (LAP) is one such semiorganic nonlinear optical material discovered by Xu et al (1983). An organic chiral molecule (L-arginine), an inorganic acentric tetrahedral molecule (phosphoric acid), and a water molecule are combined by positive-negative coulomb interactions and hydrogen bonding. It is believed that planar guanidinium and carboxylate groups at the two terminals of the L-arginine are responsible for the SHG. As for the contribution of the tetrahedral phosphate group to the NLO effect, there are still some arguments. LAP has been attracted by many researchers because of its excellent characteristics. LAP crystals are used for second, third and fourth harmonic generation from the fundamental radiation 1.06 µm and also sum and difference frequencies generation in wide spectral range from UV to IR. LAP has three times the nonlinearity, two or three times high damage threshold of KDP. LAP has high chemical stability and is less deliquescent. Since the discovery of LAP (Xu et al 1983, Eimerl et al 1989) it was considered to be a highly promising candidate for new polar materials.
L-histidine tetrafluoroborate (L-HFB) is a NLO crystal material belongs to the monoclinic system with space group \( \text{P2}_1 \). The SHG intensity of L-HFB crystal is five times that of the KDP. The transmission range of L-HFB crystal has been measured to be 250 to 1500 nm, thus green and blue light can be obtained with L-HFB single crystals. The power threshold figure-of-merit compares favourably with \( \beta \)-barium borate (BBO) and lithium triborate (LBO) single crystals. It exhibits interesting potential uses in high average powder frequency conversion in the near UV to the near IR. Besides, the L-HFB built from organic-inorganic complexes in which the high optical nonlinearity of a purely organic compound is combined with the favourable mechanical and thermal properties of an inorganic material (Aggarwal et al 2003). Therefore, single crystals of L-HFB are promising materials throughout the blue and near UV spectra region.

Literature survey shows that the research work has been performed to grow various kinds of semiorganic crystals based on organic-inorganic complexes with the aim of growing good quality crystals, understanding their growth kinetics, thermal stability, structure, linear and nonlinear optical characteristics. Mukerji et al (1998) found new semiorganic crystal: L-arginine hydrobromide (LAHBr). Petrosyan et al (2000) reported new analogs of LAP such as L-arginine dibromide and they completely characterized the crystals using infrared spectroscopy and X-ray studies. Rajan Babu et al (2003) reported the growth of L-alanine tetrafluoroborate (L-AlFB) crystals by slow evaporation. An L-AlFB crystal possesses orthorhombic structure and hexagonal morphology with slight elongation along its crystallographic c-axis. In powder form, it was found to have higher SHG efficiency than L-alanine. Haja Hameed et al (1999) examined the growth of sulfate mixed LAP (LASP) crystals, and Cu and Mg doped LAP crystals. Their hardness studies revealed that LAP crystals were harder than LASP crystals due to loosely bound sulfur in LASP crystals. Ittyachan and
Sagayaraj (2002) reported the growth of L-arginine diphosphate (LADP) having dimensions up to $30 \times 6 \times 4 \text{ mm}^3$ by slow evaporation at constant temperature of $30 \degree C$ from its aqueous solution. Pal et al (2002) reported the crystal growth of two NLO optical materials: L-arginine hydrochloride monohydrate and L-arginine hydrobromide monohydrate by slow evaporation and also by slow cooling of solution. It was found that mixed crystals are transparent down to $240 \text{ nm}$ and its SHG efficiency for $1064 \text{ nm}$ laser radiation is almost same as that of parent crystals. Laser damage threshold for mixed crystals was higher than L-arginine hydrobromide monohydrate. Ittyachan and Sagayaraj (2003) reported for the first time, successful growth of L-histidine bromide (L-HB) by slow evaporation technique. In the entire visible region of the spectra, the absorbance was found to be less than 2 units. Imparting ionic character to large NLO-response organic molecules via complexation and/or salt formation works to improve the mechanical and optical properties of the crystals of these materials and also provides a high degree of design flexibility for NLO effects. A further benefit of this approach is that semiorganic crystals are prepared by crystallization from near-ambient temperature solvents.

Evans et al (1998) have proposed that a proton transfer between two separate material species takes place and results in the increase of the hyperpolarizability of both species provided one is an acid and second is a base. An acid and a base, is a common approach to the design of materials for NLO. The acid chosen for study in this work was sulfuric acid, and the base was 2-aminopyridine. The organic molecule 2-aminopyridine, with two nitrogen atoms has often been used as ligand in metal complex (Qin et al 1999) and with nitrophenols to generate noncentrosymmetric lattice (Jaya Prakash et al 2005) that exhibits SHG. The crystal structure of the title compound bis(2-aminopyridinium) sulfate (B2APS) has reported by Jebas et al (2006). In the structure of B2APS ($2C_8H_7N_2^+\cdot SO_4^{2-}$), the S atom of the sulfate anion
lies on a twofold axis. The structure is stabilized by an extensive network of N–H···O hydrogen bonds. No efforts were made to grow larger size crystals and their physico-chemical characterization studies. The present investigation reports growth of B2APS single crystals from aqueous solution and their characterization studies.

5.2 SYNTHESIS, SOLUBILITY, METASTABLE ZONE WIDTH AND CRYSTAL GROWTH OF B2APS

For the synthesis of B2APS, saturated solutions of 2-aminopyridine (SRL, India) and sulfuric acid (Merck) were prepared separately. Then these solutions were mixed in 1:1 molar ratio at a temperature of 90 °C. The solution was stirred well for 5 h using magnetic stirrer and the pH value of the solution is 5.1. The precipitate of crystalline substance was obtained. The synthesized salt was purified by repeated crystallization processes.

Solubility studies were carried out in a CTB with cooling facility (accuracy of ± 0.01 °C). The solubility of B2APS at 30 °C was determined gravimetrically. Conventional polythermal method (Nyvlt et al 1970) was adopted for the determination of metastable zone width. The studies were repeated for different saturation temperatures 35, 40, 45 and 50 °C. Figure 5.1 shows the variation in solubility with metastable zone width at these temperatures. It reveals that solubility of B2APS is quite regular and increases with the increase in temperature in a linear way. The solubility of B2APS in water is 62.5 g/100 ml at 30 °C; it increases to 74.35 g/100 ml at 50 °C. So water is a suitable solvent for the growth of B2APS by solution growth method. The metastable zone width of B2APS in aqueous solution as a function of temperature indicates that the zone width decreases with increase in temperature.
Figure 5.1 Solubility and nucleation curves of B2APS

The saturated solution of recrystallized salt of B2APS at room temperature (35 °C) was filtered and transferred to crystal growth vessels. The crystallization was allowed to take place by slow evaporation at room temperature. The single crystals of B2APS were obtained after 28 days. Figure 5.2 shows the photograph of as–grown B2APS crystals.

Figure 5.2 Grown single crystals of B2APS
Morphology of the grown crystals was identified by the single crystal X-ray diffraction studies (Bruker Kappa APEXII). It establishes that the crystals have 8 developed faces out of which (010) and (010) are prominent. For each face, its parallel Friedal plane is also present in the grown crystal and shown diagrammatically in Figure 5.3.

![Morphology diagram of B2APS crystal](image)

**Figure 5.3 Morphology diagram of B2APS crystal**

### 5.3 X-RAY DIFFRACTION STUDIES

The unit cell parameters of grown crystal was determined by single crystal X-ray diffraction study using NONIUS CAD-4/MACH 3 diffractometer with MoK$_\alpha$ radiation in the wavelength 0.71073 Å. The cell parameters were obtained from least-squares refinement of the setting angles of 25 reflections. The determined unit cell parameters are presented in Table 5.1 in comparison with reported values (Jebas et al 2006) and it shows that they are in close agreement. It shows that the crystal belongs to the orthorhombic system with space group Fdd2.
Table 5.1 Crystal lattice parameters of B2APS

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Present study</th>
<th>Literature (Jebas et al 2006)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>12.878 (2)</td>
<td>12.873 (7)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>16.837 (4)</td>
<td>16.835 (8)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>12.041 (3)</td>
<td>12.035 (8)</td>
</tr>
<tr>
<td>α (°)</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>β (°)</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>γ (°)</td>
<td>90.00</td>
<td>90.00</td>
</tr>
<tr>
<td>System</td>
<td>Orthorhombic</td>
<td>Orthorhombic</td>
</tr>
</tbody>
</table>

The grown crystals were finely powdered and have been subjected to powder XRD analysis. Powder X-ray diffraction pattern of the grown B2APS was recorded over the range 10–60° by employing SEIFERT, 2002 (DLX model) diffractometer with CuKα (λ = 1.5405 Å) radiation using a tube voltage and current of 40 kV and 30 mA respectively. The indexed powder X-ray diffraction pattern of B2APS is given in Figure 5.4.

Figure 5.4 Powder XRD pattern of B2APS
5.4 HIGH-RESOLUTION X-RAY DIFFRACTION (HRXRD) ANALYSIS

The crystalline perfection of the grown B2APS single crystals was characterized by HRXRD by employing a multicrystal X-ray diffractometer. The rocking or diffraction curves were recorded by changing the glancing angle (angle between the incident X-ray beam and the surface of the specimen) around the Bragg diffraction peak position $\theta_B$ (taken as zero for the sake of convenience) starting from a suitable arbitrary glancing angle and ending at a glancing angle after the peak so that all the meaningful scattered intensities on both sides of the peak include in the diffraction curve. The DC was recorded by the so-called $\omega$ scan wherein the detector was kept at the same angular position $2\theta_B$ with wide opening for its slit. This arrangement is very appropriate to record the short range order scattering caused by the defects or by the scattering from local Bragg diffractions from agglomerated point defects or due to low angle and very low angle structural grain boundaries (Bhagavannarayana et al 2010).

Before recording the diffraction curve to remove the non-crystallized solute atoms remained on the surface of the crystal and the possible layers which may sometimes form on the surfaces on crystals grown by solution methods (Bhagavannarayana et al 2006) and also to ensure the surface planarity, the specimen was first lapped and chemically etched in a non preferential etchant of water and acetone mixture in 1:2 ratio.

Figure 5.5 shows the high-resolution diffraction curve (DC) recorded for a typical B2APS single crystal using (222) diffracting planes in symmetrical Bragg geometry by employing the multicrystal X-ray diffractometer with MoK$\alpha_1$ radiation. As seen in the figure, the DC contains a single peak and indicates that the specimen is free from structural
grain boundaries. The FWHM (full width at half maximum) of the curve is 19 arc s which is only slightly more than that expected for an ideally perfect crystal from the plane wave theory of dynamical X-ray diffraction (Batterman et al 1964), but close to that expected for a nearly perfect real life crystal.

![Graph](image)

**Figure 5.5** High-resolution X-ray diffraction curve recorded for a typical B2APS single crystal specimen using (222) diffracting planes

It is interesting to see the asymmetry of the DC. For a particular angular deviation ($\Delta \theta$) of glancing angle with respect to the peak position, the scattered intensity is much more in the positive direction in comparison to that of the negative direction. This feature clearly indicates that the crystal contains predominantly interstitial type of defects than that of vacancy defects. This can be well understood by the fact that due to interstitial defects (self interstitials or impurities at interstitial sites), which may be due to fast growth and/or impurities present in the raw material, the lattice around these defects undergo compressive stress (Bhagavannarayana et al 2008) and the lattice parameter $d$ (interplanar spacing) decreases and leads to give more scattered (also known as diffuse X-ray scattering) intensity at slightly higher
Bragg angles ($\theta_B$) as $d$ and $\sin \theta_B$ are inversely proportional to each other in the Bragg equation ($2d\sin \theta_B = n\lambda$; $n$ and $\lambda$ being the order of reflection and wavelength respectively which are fixed). However, the single diffraction curve with reasonably low FWHM indicates that the crystalline perfection is fairly good. The density of such interstitial defects is however very meager and in almost all real crystals including nature gifted crystals, such defects are commonly observed and are many times unavoidable due to thermodynamical conditions and hardly affect the device performance. More details may be obtained from the study of high-resolution diffuse X-ray scattering measurements (Lal et al 1989), which is however not the main focus of the present investigation. It is worth to mention here that the observed scattering due to interstitial defects is of short order nature as the strain due to such minute defects is limited to the very defect core and the long order could not be expected and hence the change in the lattice parameter of the crystal is not possible. It may be mentioned here that the minute information like the asymmetry in the DC could be possible as in the present sample only because of the high-resolution of the multicrystal X-ray diffractometer used in the present investigation.

5.5 FTIR SPECTRAL ANALYSIS

The FTIR spectrum of B2APS was recorded using a Perkin-Elmer FTIR spectrum RXI spectrometer by KBr pellet technique. The recorded FTIR spectrum in the range 400–4000 cm$^{-1}$ at room temperature is shown in Figure 5.6. The band at 3312 cm$^{-1}$ is assigned to NH symmetrical stretching in NH$_2$. C–H symmetrical stretching is observed at 3156 cm$^{-1}$. The band at 1664 cm$^{-1}$ is attributed to C=N stretching. The peaks at 1623 and 721 cm$^{-1}$ represents the C=C stretching and C–C out-of-plane bending of the aromatic ring respectively. C–C stretching in the ring is assigned to the band at 1548 cm$^{-1}$. The peaks at 1479 and 1382 cm$^{-1}$ are due to C=N and C–NH$_2$
stretching in the ring. The strong absorption at 1121 cm\(^{-1}\) is assigned to the asymmetric stretching of SO\(_4\). The band at 1324 cm\(^{-1}\) corresponds to C–NH\(_2\) stretching in 2-aminopyridine. The presence of SO\(_4^{2-}\) is revealed by the bands observed at 994 and 619 cm\(^{-1}\) (Nakamoto 1970). The strong absorption at 768 cm\(^{-1}\) confirms the aromatic ring in the compound. The characteristic stretching vibration of sulfate ion appeared at 877 cm\(^{-1}\).

![Figure 5.6 FTIR pattern of B2APS](image)

### 5.6 THERMAL STUDIES

The thermal stability of B2APS was identified by thermogravimetric and differential thermal analysis simultaneously. The studies were conducted by TA instrument Model Q600 SDT thermal analyzer in an atmosphere of nitrogen at a heating rate of 10 °C/min and the TGA-DTA curves are illustrated in Figure 5.7. The endothermic peak at 210 °C in DTA inferred that the melting point of the material occurs. The absence of crystallization of water in the molecular structure of B2APS was identified by the absence of weight loss around 100 °C in TGA response. The weight loss starts around 176 °C and no endothermic or exothermic peaks exists below
this temperature. It means the absence of any isomorphic phase transition in
the sample. The shoulder peaks in the curve after the melting point
 corresponds to the decomposition of the material.

![Graph showing TGA-DTA curves of B2APS](image)

**Figure 5.7 TGA-DTA curves of B2APS**

### 5.7 DIELECTRIC MEASUREMENTS

Practically, the presence of a dielectric between the plates of a
condenser enhances the capacitance. Essentially, dielectric constant \( \varepsilon_r \) is the
measure of how easily a material is polarized in an external electric field.
Conventional parallel plate capacitor method was employed to determine the
capacitance \( (C_{\text{crys}}) \) and dielectric loss (\( \tan \delta \)) of B2APS crystal at the
frequency range 100 Hz to 1 MHz using the Agilent 4284A LCR meter at
temperatures ranging from 313 to 353 K. The sample of 2 mm thickness was
prepared from the transparent part of the crystal and both its surfaces were
coated by graphite paste to make a contact with the electrodes. The plot of
dielectric constant against log frequency at different temperatures is shown in
Figure 5.8.
It is observed from the figure that the dielectric constant decreases with increasing frequency and then attains almost a constant value in the high frequency region. It is also shows that as the temperature increases, the value of the dielectric constant also increases. At 353 K, the dielectric constant of B2APS crystal at 100 Hz is 6.72, and this value decreases to 2.46 at 1 MHz. The dielectric constant is maximum at 100 Hz since all the types of polarization such as electronic, ionic, orientation and space charge polarizations occur at lower frequency. Because of the inertia of the molecules and ions at high frequencies, the orientation and ionic contribution of polarization are small (Kittel 1993). So, the magnitude of polarization increases with the decrease of frequencies. The variation of dielectric loss against frequency at different temperatures shown in Figure 5.9 also reveals the same behavior. The characteristic of low dielectric constant and dielectric loss with high frequency suggests that the crystal possess enhanced optical quality with lesser defects (Benet et al 1994).
5.8 UV–vis–NIR SPECTRAL STUDIES

The optical spectrum of B2APS was recorded with Lambda 35 spectrophotometer in the range 200–1100 nm with a crystal of thickness 1.5 mm. The UV–vis–NIR spectrum shown in Figure 5.10 indicates that the crystal has wide transmission of above 60% in the entire range. The cutoff wavelength of B2APS is 353 nm and there is no absorption band between 353 and 1100 nm; hence the crystal is expected to be transparent between these two wavelengths.
5.9 NLO PROPERTY

Quantitative measurement of relative SHG efficiency of B2APS with respect to well known SHG material KDP was made by the Kurtz and Perry powder technique. Nd: YAG laser (DCR11) was used as a light source. A laser beam of fundamental wavelength of 1064 nm, 8 ns pulse width, with 10 Hz pulse rate was made to fall normally on the sample cell. The input laser energy incident on the powdered sample was chosen to be 11.5 mJ/pulse. The doubling of frequency was confirmed by the green color of the output radiation whose characteristic wavelength is 532 nm. The SHG signal of 130 mV was obtained for B2APS, while the KDP gave an SHG signal of 50 mV for the same input beam energy. Thus relative SHG conversion efficiency of B2APS is 2.6 times that of KDP.

5.10 CHEMICAL ETCHING STUDIES

The presence of dislocations in a crystal influence a number of physical properties like plasticity, mechanical strength etc. Hence it is necessary to study the distribution and density of dislocations in a crystal. In the present investigations, chemical etching technique has been employed to study dislocations in B2APS crystals using Magnus MLX microscope fitted with Motic (1000) camera. Care has been taken to ensure that no microcrystals were present on the surface before treated with chemicals. Among the various etchants used, the best etching action was observed with methanol. Figures 5.11 and 5.12 show the successive etch pit patterns on (010) face of B2APS crystal with methanol as etchant for etching timings 2 and 4 s respectively. It reveals that the etch pits are more or less rectangular in shape, suggesting two fold rotational symmetry of the face. It can be clearly seen from these photographs that all the etch pits in Figure 5.11 persist in Figure 5.12 with increase in size indicating that etch pits are formed at dislocation sites only. The average etch pit density (EPD) is found to be
$0.75 \times 10^5 \text{ cm}^{-2}$. The distribution of etch pits is not uniform. The statistical study of 20 crystal samples of B2APS reveals more etch pit density at the edges of the crystals. This may be due to initiation of the growth layers from edges.

Figure 5.11 Etch pattern produced on (010) face of B2APS crystal by methanol after etching for 2 s

Figure 5.12 Etch pattern produced on (010) face of B2APS crystal by methanol after etching for 4 s

5.11 MECHANICAL HARDNESS MEASUREMENTS

The microhardness characterization is extremely important as far as the fabrication of devices is concerned. Hardness of a material is a measure of the resistance it offers to local deformation. Vickers microhardness
measurements on (010) face of B2APS crystal were made using Leitz-Wetzlar microhardness tester fitted with a Vickers diamond pyramidal indenter. The measurements were made at room temperature and the indentation time was kept at 10 s. Microhardness value was taken as the average of the several impressions made. The variation of Vickers hardness number ($H_v$) with load in the range 10–100 g is depicted in Figure 5.13.

![Figure 5.13 Plot of Vickers microhardness number versus load](image)

It shows that hardness value increases rapidly with increase of load up to 70 g and beyond which it increases slowly. At low loads, the indenter penetrates only the top surface layers generating dislocations, which results in the increase of hardness in this region. The slow increase of hardness at higher loads can be attributed to the mutual interaction or rearrangement of dislocations (Raja Shekar et al 2009).

5.12 CONCLUSIONS

Nonlinear optical material bis(2-aminopyridinium) sulfate was synthesized and single crystals were grown by slow solvent evaporation
technique. The unit cell parameters of the crystal were confirmed by single crystal X-ray diffraction analysis. The solubility and metastable zone width were determined. Thermal studies show that B2APS crystal melts at 210 °C. The dielectric constant and dielectric loss of B2APS crystal at different frequencies and temperatures were determined. Mechanical studies reveal that Vickers microhardness number increases with applied load. Chemical etching analysis on (010) face of B2APS crystal suggests two fold rotational symmetry of the face. Linear optical spectrum elucidates that B2APS crystal has good transmission window between 353 and 1100 nm. The SHG relative efficiency of B2APS was found to be 2.6 times that of KDP.