CHAPTER VI
GROWTH ANISOTROPIC AND CHARACTERIZATION OF
ANILINIUM PERCHLORATE SINGLE CRYSTAL

6.1 INTRODUCTION

Nonlinear optical (NLO) materials are capable of producing higher harmonics and find applications in optical modulation, fiber optic communication and opto-electronics (Yu and Xue, 2006; Dongfeng Xue and Siyuan Zhang, 1999). In recent years, many researchers have put their effort to find variety of NLO crystals for laser applications. Inorganic crystals are widely used in aforementioned applications because of their high melting point, high mechanical stability and high degree of chemical inertness. The availability of suitable optical nonlinear inorganic crystals is generally lower than the optical device demand. Organic compounds are often formed by weak Van der Waal’s, hydrogen bonds and possess a high degree of delocalization which is responsible for NLO crystals (Dongli Xu and Dongfeng Xue, 2008; Xiue Ren and Dongli Xu, 2008; Dongfeng Xue and Henryk Ratajczak, 2003; Dongfeng Xue and Siyuan Zhang, 1999; Keyan Li et al., 2008). A major drawback of organic NLO crystals is the difficulty in growing large size crystal with good optical quality and higher physico-chemical stability. Nonlinear optical properties of semi-organic materials are currently under intense investigation, triggered by potential applications in NLO due to their incorporated advantages of both organic and inorganic crystals (Newman et al., 1990). Perchloric acid is an inorganic compound with the formula, HClO$_4$ stronger than sulfuric and nitric acids. Aniline, an aromatic amine and a phase transition dielectric material, attractive for NLO and memory storage applications (Hoong-Kun Fun et al., 2011). Recently, similar structures containing anilinium cations have been reported. Among examples, can be named the following ones: anilinium nitrate (Rademeyer, 2004), anilinium picrate (Smith et al., 2004), anilinium hydrogenphosphite and anilinium hydrogenoxalate hemihydrates (Paixao et al.,
2000). In the present investigation, first time we report, different habit, anisotropic studies, NLO study and Z- scan study of AP single crystals for nonlinear optical applications.

6.2 MATERIAL SYNTHESIS

The pure AP material was synthesized from a saturated solution of water containing aniline and perchloric acid in 1:1 stoichiometric ratio by the following reaction,

\[
\text{Aniline} + \text{HClO}_4 \rightarrow \text{Anilinium perchlorate (AP)}
\]

6.3 SOLUBILITY

Solubility of the purified AP material in the selected solvents, such as n-hexane, acetonitrile, toluene, acetone, ethanol, methanol and water were determined in the temperature range between 30°C and 50°C in steps of 5°C by gravimetric method.

![Figure 6.1 Solubility of AP in different solvents](image)

Digitally controlled constant temperature bath having temperature controlling accuracy of ±0.01°C was used for this study. Saturated solution of AP with one of
the above selected solvents at a specified temperature was prepared in an air-tight round bottom flask with ground sleeve stirrer glands attachment for effective stirring with immersible magnetic stirrer. The synthesized salt was dissolved in respective solvent to prepare the solution at a temperature slightly above the chosen constant temperature of 35ºC. The prepared solution was continuously stirred using a motorized magnetic stirrer to ensure homogeneous temperature and concentration over the entire volume of the solution. The saturated solution was kept at a particular chosen temperature for about 6 hours to attain equilibrium. The as prepared AP solution of 10 mL was taken in a warm pipette and poured into petridish. The experiment was repeated for all temperatures. The solubility curves for AP in various solvents are given in figure 6.1.

The solubility studies made for AP with different solvents selected in the present study implies that the material has lower solubility in the non-polar solvents and higher solubility in the polar solvents. Moreover, it is observed that the solubility of AP increases with the polarity of the solvents used. Accordingly, the ascending order of solvents with respect to the solubility of AP is given as: n-hexane < acetonitrile < toluene < acetone < ethanol < methanol < water. The solubility of AP in water is moderate throughout the temperatures studied. This indicates that water will be a suitable medium with moderate solubility to perform the growth of good quality AP crystal by both by slow evaporation and slow cooling methods.

Meta stable zone width, solution stability indicator, can be experimentally measured. It is influenced by the factors, such as stirring rate, cooling rate of the solution and presence of additional impurities. The meta stable zone width of AP for water was determined by poly thermal method (Vivek and Murugakoothan, 2015). The aqueous AP solution saturated at 30ºC was prepared according to the solubility data and filtered using Whatman filter paper. The pure aqueous AP solution was kept in a constant temperature water bath and stirred continuously for a period of 6 hours for homogenization. The solution was slowly cooled, until the
first speck appeared and it was instantly recorded as the nucleation temperature. The difference between the saturation and nucleation temperature gives the metastable zone width of the AP in water. The experiment was repeated for different saturation temperatures, like 35, 40, 45 and 50°C (Vivek and Murugakoothan, 2013). The nucleation curve is drawn and is shown in figure 6.2.

![Nucleation Curve](image)

**Figure 6.2 Metastable zone width of AP in water**

### 6.4 CRYSTAL GROWTH

Saturated solutions of AP at room temperature was prepared with each of the seven solvents, such as n-hexane, acetonitrile, toluene, acetone, ethanol, methanol and water separately, filtered twice with Whatman filter paper and taken in separate beakers. The beakers were covered with aluminium foil and perforations were made equally and uniformly on all of them. All the crystallizing beakers were kept in a dust free ambience maintained at room temperature. Nucleated crystals were allowed to grow for definite period equally and then harvested. Uniform condition was maintained while growing crystals from the solutions prepared from different solvents. Photographs of the grown AP crystals having different habits from solutions with above mentioned solvents are shown in figure 6.3. The schematic drawings of the habits of the grown crystals with
identified faces by single crystal X-ray diffraction study are given in figure 6.3. When the habit of the grown AP crystals was examined, as shown in figure 6.3, it is clear that the habit differs from solvent to solvent. Six major classifications can conveniently be made on them: needle, platelet, bar, pyramidal cuboid, pyramidal cubic square and cuboid.

6.4.1 Crystal Growth from Non-polar Solvents

n-hexane

Among the two non-polar solvents used in this study, n-hexane yielded only needle like crystals. Needles are elongated several millimeters (~15 mm long) along the (2 0 -1) direction and having square cross section 0.5 x 0.5 mm² with prominent (0 0 1) plane as shown in figure 6.3(a). With n-hexane, as a result of high evaporation rate at room temperature and comparatively with less solubility for AP, we could obtain only this type of needle like crystals in all our experiments carried out at different occasions. It is clear from this observation that the AP crystal exhibit unidirectional growth behavior in the n-hexane solvent. Hence, bulk crystals of AP can be grown from n-hexane solvent by properly restricting the growth along (2 0 -1) direction and also encouraging the growth along (0 0 1) direction.

Toluene

The solution prepared with toluene yielded crystals with elongated rectangular bar morphology. Every bar type crystal has dimension about 20 mm along its (2 0 -1) direction, about 1 mm along its (0 1 0) direction and about 1.5 mm along (0 0 1) direction. The surfaces of faces of these crystal bars are found to be rough and are shown in figure 6.3(b). Though toluene has moderate evaporation rate at room temperature, its less polar nature with dipole moment of 0.36 debye and with low solubility characteristics for AP, it yielded only crystals having rectangular bar morphology with poor quality from all of our attempts in the present study.
Figure 6.3 Photograph and morphology of the AP crystals grown from different solvents, (a) n-hexane, (b) toluene, (c) acetonitrile, (d) acetone, (e) ethanol, (f) methanol and (g) water
Though toluene has moderate evaporation rate at room temperature, its less polar nature with dipole moment of 0.36 debye and with low solubility characteristics for AP, it yielded only crystals having rectangular bar morphology with poor quality from all of our attempts in the present study.

6.4.2 Crystal Growth from Polar Solvents

Acetonitrile

The polar solvent acetonitrile yielded needle type AP crystals. In this case the needles are of columnar type which extended for about 16 mm long along its (2 0 -1) direction and about 0.5 - 1 mm along both of its (0 0 1) as well as (0 1 0) directions. The grown crystal has only one prominent face (0 0 1) as shown in figure 6.3(c).

Acetone

Acetone is a highly polar solvent when compared to the other solvents used in this study. Its evaporation rate is high at room temperature. The solubility of AP in acetone is also comparatively large. These factors just favor the growth of only small crystals and we observed the same in all our attempts by solvent evaporation method. Cuboid shaped AP crystal elongated several millimeters (~16 mm long) along the (2 0 -1) and about 6 mm along both of its (0 0 1) and (0 1 0) directions were obtained while using acetone as solvent. The crystal has been grown out with the prominent face (0 0 1) as shown in figure 6.3(d).

Ethanol

The solution prepared with another polar solvent ethanol also yielded crystals with three-dimensional distorted pyramidal cuboid like morphology. But the growth along its (2 0 -1) direction is higher than that of (0 1 0). The crystal has extended about 8 mm along its (2 0 -1) direction, 6 mm along its (0 1 0) direction and about 2 mm along its (0 0 1) direction as shown in figure 6.3 (e). The overall size and quality of the AP crystals grown using methanol as solvent is good while compared with that of the aforementioned solvents. This may be attributed to less evaporation rate at room temperature and good solubility of AP in ethanol.
Methanol

The polar solvent methanol yielded crystals of comparatively smaller dimensions with pyramidal cubic square. The prism faces, such as (0 0 1), (2 0 -1), (0 1 0), (0 -1 0) and (-2 0 1) are existing with smaller dimensions. The crystal has extended for about 6 mm along its (2 0 -1) direction and about 6 mm along its (0 1 0) and (0 0 1) directions as shown in figure 6.3(f). Methanol exhibiting moderate evaporation rate at room temperature and having moderate solubility for AP, yielded small crystals of good quality and are transparent without any visible defects.

Water

The solution prepared with water yielded crystals of AP with cuboid shape. The (0 0 1) plane forms common edge with different faces, such as (0 0 1), (2 0 -1), (0 1 0), (0 -1 0) and (-2 0 1). The crystal has been grown out about 33 mm long along its (2 0 -1) direction, about 5 mm along its (0 0 1) direction and about 4 mm along its (0 1 0) direction as shown in figure 6.3(g). The quality and size of the resulted crystals are also very good. Water with highest polar nature and highest solubility for AP among the solvents used in the present study and comparatively less evaporation rate yielded good quality single crystals in all our growth experiments performed at different occasions. From the above six solvents used, water is found to be a very good solvent and suitable for AP crystal growth. As an overall assessment, different solvents used in the present study influence the growth rate and morphology of AP crystal. In addition, AP crystal has large growth rate in the (2 0 -1) direction in all the growth experiments conducted in the present study irrespective of the solvents used. This growth rate anisotropy has been reported in some other nonlinear crystals recently (Srinivasan and Sherwood, 2005; Srinivasan and Arumugam, 2007; Srinivasan, 2008) and AP crystal also behaves in a similar way.
6.5 GROWTH FROM SOLVENT SLOW EVAPORATION TECHNIQUE

The AP crystal was grown by seed submerged method. The seed crystals were optically transparent with well defined edges. After careful selection of the seed crystals, they were immersed into the mother solution using nylon thread to encourage further growth of bulk size crystals. Well defined and transparent crystals were grown in 32 days by slow solvent evaporation technique at room temperature. The optically transparent rectangular shape brown colour AP crystal grown by this method is shown in figure 6.4(a). The AP crystal is non-hygroscopic nature.

![Image](image_url)

**Figure 6.4** (a) As grown AP crystal, (b) Morphology of AP crystal; Cut and polished pieces of (c) (0 0 1) plane, (d) (0 1 0) plane, (e) (2 0 -1) plane

6.6 CHARACTERIZATION STUDIES

6.6.1 X-Ray Diffraction

The single crystal XRD study reveals that the title material belongs to orthorhombic crystal system with non-centrosymmetric space group P2₁2₁2₁ and the unit cell parameters are, a = 5.891 Å, b = 7.477 Å, c = 18.987 Å and volume of the unit cell is found to be 639.64 Å³.

The figure 6.5 shows the high resolution diffraction curve (DC) recorded or AP specimens using (0 0 2) diffracting planes in symmetrical Bragg geometry.
with Mo Kα₁ radiation. The rocking curves for acetone, ethanol, methanol and water are shown in figures 6.5(a), 6.5(b), 6.5(c) and 6.5(d) respectively. The curves are reasonably sharp having full width at half maximum (FWHM) of 67.8 arc s., 69.9 arc s., 69.8 arc s. and 65.7 arc s. for AP crystal grown using acetone, ethanol, methanol and water as solvents respectively. The HRXRD curves indicating a nearly perfect crystal from the plane wave dynamical theory of XRD (Dederichs, 1973). The observation of slightly higher FWHM may be attributed to the incorporation of acetone, ethanol, methanol and water in the crystalline matrix of AP. Absence of additional peaks confirms that the specimens crystal do not contain any internal structural grain boundaries (Magesh et al., 2011) and indicates that the crystalline perfection is quite good. The lower FWHM of DC is the indicator of quality of the crystal. Hence, it is clear from the HRXRD study, AP crystal grown from water is better than that of the AP crystals grown from other solvents.

**Figure 6.5 X-ray rocking curve of AP crystal grown from (a) ethanol, (b) methanol, (c) acetone and (d) water**
6.6.2 Thermal Study

The thermal behaviour of AP was studied by thermograviemetric analysis (TG) and differential thermal analysis (DTA) using the AP sample of 10 mg at the beginning grown from water solvent. A thermal analyzer was employed at a heating rate of 10°C/min. in the nitrogen atmosphere. The TG and DTA thermograms recorded in the temperature range 30-600°C are shown in figure 6.6. The DTA trace illustrates an endothermic phase transition at 268°C and is assigned to decomposition of the sample by thermal breaking of bonds of the sample. It is observed from the TG trace that a major weight loss occurs at 268°C in a single step. From the thermal study, it can be inferred that AP crystal may be exploited for NLO applications up to around 268°C. The sharpness of the TG trace at the decomposition can be attributed to a good degree of crystallinity and single phase of the grown AP crystal.

Figure 6.6 TG-DTA thermograms of AP
6.6.3 Hardness

Microhardness study of any system has direct correlation with the crystal structure and is very sensitive to the presence of other phases or phase transition prevalent in the system. The Vicker’s microhardness number is calculated using the following relation,

\[ H_v = \frac{1.8544 \ P}{d^2} \]  

(6.1)

where ‘\( H_v \)’ is the Vicker’s hardness number, ‘\( P \)’ is the applied load and ‘\( d \)’ is the average diagonal length of the indentation mark. Indentations were made on the \((0 \ 0 \ 1)\), \((0 \ 1 \ 0)\) and \((2 \ 0 \ -1)\), prominent faces of the sample at different temperature.

The microhardness measurement was made for the applied loads varying from 10 to 80 g for \((0 \ 0 \ 1)\) plane, 10 to 70 for \((0 \ 1 \ 0)\) plane and 10 to 50 for \((2 \ 0 \ -1)\) plane for the dwell time 15 s using Reichert Polyvar 2 MET microscope. Since AP crystal starts decomposing at 268°C the samples were heat treated only up to 250°C. Separate plots between the hardness number and the load at different temperatures are depicted in figure 6.7(a), 6.7(b) and 6.7(c) for the planes \((0 \ 0 \ 1)\), \((0 \ 1 \ 0)\) and \((2 \ 0 \ -1)\) planes respectively. From the hardness value, the yield strength, \( \sigma_y \) and elastic stiffness constant (\( C_{11} \)) were calculated and this follows the same trend as that of the BAP crystal explained in chapter 3. The yield strength at room temperature for planes \((0 \ 0 \ 1)\), \((0 \ 1 \ 0)\) and \((2 \ 0 \ -1)\) is found to be 41.31 MPa, 39.42 MPa and 37.42 MPa respectively. The trends of stiffness constant graph is similar to that of hardness number graph and are shown in figures 6.7(d), 6.7(e) and 6.7(f) for the planes \((0 \ 0 \ 1)\), \((0 \ 1 \ 0)\) and \((2 \ 0 \ -1)\) planes respectively.
Figure 6.7 Plot of Hardness number vs Load of (a) (0 0 1) plane, (b) (0 1 0) plane (c) (2 0 -1) plane and Plot of load vs stiffness constant of (d) (0 0 1) plane, (e) (0 1 0) plane, (f) (2 0 -1) plane
6.6.4 UV–vis–NIR Spectral Study

The cut and polished AP crystal plates of thickness 2 mm were used for UV–vis–NIR spectral study and the spectra obtained are shown in figure 6.8.

![UV–vis–NIR transmission spectra of AP](image)

**Figure 6.8 UV–vis–NIR transmission spectra of AP**

The AP (0 0 1), (0 1 0) and (2 0 -1) plane of AP crystal cut plates are optically transparent in the entire visible region with 86 %, 82 % and 80 % transmittance respectively and lower cut-off wavelength of 383 nm and is shown in figure 6.8. The optical reflectance of (0 0 1), (0 1 0) and (2 0 -1) plane cut plates of AP crystal of in the entire visible region is about 11 %, 16 % and 20 % respectively and is shown in figure 6.9.
6.6.5 Refractive Index

The refractive index of cut and polished AP crystal \((0 0 1)\), \((0 1 0)\) and \((2 0 -1)\) plane cut plates of AP crystal was measured by the Metricon Model 2010/M Prism coupler using the wave length of 632 nm. The sample was clamped against the prism and index was determined by measuring critical angle \(\theta\) for the sample interface. A laser beam strikes the base of the prism and is normally reflected at the prism base onto a photo detector. The refractive indices of \((0 0 1)\), \((0 1 0)\) and \((2 0 -1)\) planes of AP crystal are 1.610, 1.614 and 1.6126 respectively.

6.6.6 Laser Damage Threshold

The cut and polished smooth \((0 0 1)\), \((0 1 0)\) and \((2 0 -1)\) plane cut plates of AP crystal was mounted on the crystal holder in the path of the Nd:YAG laser beam and the energy of the beam was increased from 5 mJ. The crystal was exposed to laser beam for a time period of 10 ns for all measurements. The spot

![Figure 6.9 UV–vis–NIR Reflectance spectra of AP](image-url)
size of the laser beam was fixed as 1 mm. The surface damage threshold of the crystal in different planes was calculated using the expression,

\[ P = \frac{E}{\tau \pi r^2} \]  \hspace{1cm} (6.2)

where ‘E’ is the energy (mJ), ‘\(\tau\)’ is the pulse width (ns) and ‘r’ is the radius of the spot (mm). The multiple shot laser damage threshold (LDT) studies was carried out on the prominent planes (0 0 1), (0 1 0) and (2 0 -1) of AP crystal. The LDT values of AP crystal for (0 0 1), (0 1 0) and (2 0 -1) planes are determined as 0.82 GWcm\(^2\), 0.41 GWcm\(^2\) and 0.36 GWcm\(^2\) respectively. Figure 10(a), 10(b) and 10(c) shows the optical micrograph of the damage profile observed on three prominent planes, such as (0 0 1), (0 1 0) and (2 0 -1) respectively.

![Figure 6.10 Laser damage picture of (a) (0 0 1) plane, (b) (0 1 0) plane and (c) (2 0 -1) plane](image)

6.6.7 Second Order Nonlinear Optical Study

The SHG effective nonlinearity of AP crystalline powder was determined using Kurtz and Perry powder technique. It enables to measure the SHG effective nonlinearity of new materials relative to standard potassium dihydrogen phosphate (KDP). A Q-switched Nd:YAG laser operating at 1064 nm and 8 ns pulse width with an input repetition rate of 10 Hz and energy 31 mJ/pulse was used for this study. The second harmonic signal of 31 mV was obtained for AP crystal, while the standard potassium dihydrogen phosphate (KDP) crystal gives a SHG signal of 11 mV for the same input energy. It shows that the SHG effective nonlinearity of
AP is 2.8 times that of standard NLO material KDP. The particle size dependency of SHG intensity was studied. The continuous increase of SHG with increase of particle size and gets saturated confirms the phase matching behavior of the material (Vivek and Murugakoothan, 2013) and similar to the BAP crystal (Chapter 3). The particle size dependency of SHG intensity in AP is shown in figure 6.11.

![Figure 6.11 Particle size (μm) vs SHG output (mV)](image)

**Figure 6.11 Particle size (μm) vs SHG output (mV)**

### 6.6.8 Purity Dependent SHG Study

Second order NLO materials efficiency measurement was carried out using a powder SHG technique to identify the materials with non-centrosymmetric crystal structure. A Q-switched Nd:YAG laser operating at 1064 nm and 8 ns pulse width with an input repetition rate of 10 Hz and energy 31 mJ/pulse was used for this study. The second harmonic signal generated in the crystalline sample was confirmed from the emission of green radiation of wavelength 532 nm from the crystalline powder. The SHG output was converted into electrical signal and was displayed on a digital storage oscilloscope. The optical signal incident on photo multiplier tube was converted into voltage output. From this figure 6.12
SHG effective nonlinearity of AP crystal grown from water is higher than that of the AP crystal grown from other solvents.

This may be attributed that the SHG effective nonlinearity increases with quality of the crystal. As the purity of the crystal increases, SHG output also increases and it is clearly shown in figure 6.12. The SHG effective nonlinearity of AP crystal grown from water is 2.8 times that of standard NLO material KDP.

6.6.9 Z-Scan Measurements

The Z-scan is a simple and traditional experimental method to measure the intensity dependent third order nonlinear susceptibility of the materials. It allows the simultaneous measurement of both the nonlinear refractive index and the nonlinear absorption coefficient. Figure 6.13(a) illustrates the Z-scan data for the closed aperture set up for AP single crystal on (0 0 1) plane. The peak followed by a valley transmittance is the signature for negative nonlinearity (Shettigar et al., 2007). This is known as self defocussing effect which is due to local variation of refractive index with temperature. Figure 6.13(b) depicts the open aperture curve of AP single crystal. The estimated nonlinear refractive index ($n_2$), change in
refractive index ($\Delta n$), absorption coefficient ($\beta$) and third order susceptibility ($\chi^{(3)}$) values were calculated and similar to the BAP crystal (Chapter 3) and are given in table 6.1.

![Graph showing normal transmittance as a function of Z position with closed and open apertures.](image)

**Figure 6.13** Plot of normal transmittance as a function of Z position (a) with closed aperture and (b) with open aperture.

### Table 6.1 Nonlinear optical parameters of AP crystal

<table>
<thead>
<tr>
<th>Nonlinear refractive index, $n_2$ (cm$^2$/W)</th>
<th>Change in refractive index, $\Delta n$</th>
<th>Absorption coefficient, $\beta$ (cm/W)</th>
<th>Third order susceptibility, $\chi^{(3)}$ (esu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-3.82 x 10^{-6}</td>
<td>-1.03 x 10^{-3}</td>
<td>0.0396 cm/W</td>
<td>2.132 x 10^{-4}</td>
</tr>
</tbody>
</table>

**6.7 CONCLUSION**

The nonlinear optical anilinium perchlorate crystal was grown from seven different solvents. Among the seven solvents (n-hexane, acetonitrile, toluene, acetone, ethanol, methanol and water) used in the present study water with its modest polarity, moderate solubility for AP found to be more suitable for the growth of AP single crystal. The meta stable zone width of AP was determined in water. It is found that the effect of solvents on the habit of the AP crystal is very strong. As a result, solvents of different chemical nature and polarity affect crystal quality and consequently yielded crystals with different habits. The quality of the AP crystal examined by HRXRD study indicates that the crystalline quality is...
reasonably good without having any internal structural grain boundary. The thermal study inferred that AP crystal may be exploited for NLO applications up to around 268°C. Hardness measurement shows that AP crystal is mechanically stable up to 80 g. An optical study shows that the crystal has wide transmission range with UV cut-off wave-length at 383 nm. The refractive indices of (0 0 1), (0 1 0) and (2 0 -1) planes of AP crystal are 1.610, 1.614 and 1.6126 respectively. The multiple shot laser damage threshold confirms that the (0 0 1) plane posses more stability than of other planes. The (0 0 1) plane is found superior than the other planes in terms of linear optical properties, laser damage threshold and hardness. The powder SHG effective nonlinearity of this material is 2.8 times that of KDP. This shows that AP crystal grown in water has good crystalline perfection compared to the other solvents. The SHG effective nonlinearity of AP crystal grown from water is 2.8 times that of standard NLO material KDP. When the purity of crystal increases, the SHG effective nonlinearity also increases. As a result of this study it is concluded that water is a promising solvent for the growth of good quality AP crystal suitable for nonlinear optical applications. Third order nonlinear optical studies showed that the AP crystal has self - defocusing nature with nonlinear refractive index and nonlinear absorption coefficient. Owing to all these properties, AP crystals could be a promising material for the nonlinear optical applications.