CHAPTER 2

SYNTHESIS, CRYSTAL GROWTH AND CHARACTERIZATION OF AN ORGANIC NLO MATERIAL: BIS(2-AMINOPYRIDINIUM) MALEATE

2.1 INTRODUCTION

The design and synthesis of organic molecules exhibiting second order nonlinear optical properties have been motivated by the tremendous potential for their applications in the fast developing domains of optoelectronics and photonic technologies. The relevance of the organic materials in the present context is, the delocalized electronic structure of $\pi$–conjugated organic compound offers a number of tantalizing opportunities in the applications as nonlinear optical materials. Organic crystals in terms of nonlinear optical properties possess advantages when compared to their inorganic counterparts (Zyss 1993, Russell et al 1997). Generally, organic materials allow fine-tuning of their chemical structures and properties for the desired nonlinear optical properties (Datta et al 2003). In addition, they also have large structural diversity. The properties of organic compounds can be refined using molecular engineering and chemical synthesis (Matos Gomes et al 2000). Hence they are projected as forefront candidates for fundamental and applied investigations.

The design of organic polar crystals for the quadratic NLO applications is supported by the observation that organic molecules containing $\pi$ electron systems asymmetrized by electron donor and acceptor groups are
highly polarizable entities (Pecaut et al 1993). Donor/acceptor benzene derivatives are sure to produce high molecular nonlinearity. An organic molecule should possess large second order hyperpolarizability ($\beta$) to exhibit good nonlinear optical properties. Extension of benzene derivatives has permitted an increase in the number of $\pi$ electrons as well as their delocalization length, so as to lead to prodigious enhancement in $\beta$. The structural flexibility of the organic molecules are easily modifiable through precise chemical syntheses in view to increase the molecular hyperpolarizability $\beta$ and the possible grafting of chirality centers are remarkable assets compared to the difficulties of the engineering route of inorganic materials in which the requirements of noncentrosymmetry and high susceptibilities $\chi^{(2)}$ have to be accounted at the crystal form (Marder et al 1991). An essential condition to realize even-order NLO processes in materials is a noncentrosymmetric structure; however, optimal molecular orientations are required if appreciable effects are to be achieved in molecular materials (Nie 1993, Marks et al 1995).

In order to achieve good macroscopic nonlinear response in organic crystals, one requires an increase in the number of $\pi$ electrons and $\pi$ delocalization length, so as to lead to high molecular hyperpolarizability and also proper orientation of the molecule in the solid-state structure to facilitate high-frequency conversion efficiency. Effective materials generally contain donor and acceptor groups positioned at either end of suitable conjugation path. The increased effective conjugation and the large $\pi$ delocalization length have been recognized as the factors leading to the large order nonlinearities. Acentric molecules consists of highly delocalized $\pi$ electron systems interacting with suitably substituted electron donor and acceptor groups exhibit a high value of second order polarizability, $\beta$. For efficient SHG, one requires a highly polarizable $\pi$ conjugated molecule substituted with strong electron donor and acceptor groups at the ends of the molecule and also its
noncentrosymmetric crystal structure. So far, many organic Donor–π–Acceptor (D–π–A) type compounds have been studied theoretically and also experimentally (Ravindra et al 2008). The studies indicate that the organic D–π–A compounds are highly promising candidates for NLO applications.

Literature study shows that organic D–π–A type compounds with pyridinium acceptor shows large second harmonic nonlinearity (Mashraqui et al 2004). Pyridine, a simple aromatic heterocyclic organic compound, is structurally related to benzene, with one CH group replaced by a nitrogen atom. The molecule 2-aminopyridine 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 second harmonic generation. 2-aminopyridine, a heterocyclic molecule, with two nitrogen atoms may also be used as a model compound for understanding nucleic acid bases.

2.2 SURVEY OF RECENT WORKS

Bis and Zaworotko (2005) determined single crystal structures of new ionic compounds which contain both a 2-aminopyridine and a carboxylic acid moiety. Proton transfer occurs to the aromatic nitrogen of the 2-aminopyridine moiety in all these compounds. Bhuvana et al carried out the optical characteristics of crystals of 2-aminopyridinium p-nitrobenzoate (Bhuvana et al 2007) and 2-aminopyridinium p-amino benzoate (Bhuvana et al 2007 a). Both these crystals exhibit good optical transparency throughout the entire visible region. The compound 2-aminopyridinium p-nitrobenzoate synthesized by the chemical reaction of 2-aminopyridine with nitrobenzoic acid has optical band gap of 3.53 eV. In 2-aminopyridinium p-amino benzoate, nitro group is replaced with the amine group in the para position of the benzoic acid. They are reported that the replacement of the substitutional
functional group in the aromatic acid leads to the increase in the band gap of the compound from 3.53 eV and 4.13 eV. Bhuvana et al (2010) had made an attempt to enhance the optical properties further by chelating the metal binding within the compound. They selected noble metal silver in the form of silver nitrate to react with 2-aminopyridine. The optical transmittance data of 2-aminopyridinium nitrate silver reveals the maximum transparency because of its wide band gap around 4.738 eV and the less static dielectric constant of 0.851 due to silver binding suggests the suitability of this material towards the application for optoelectronic devices. The crystal structure of the complex of 2-aminopyridine and maleic acid in stochiometrical equimolar ratio was reported by Chitra et al (2008) and the structure of 2-aminopyridinium 4-nitrophenolate 4-nitrophenol was reported by Jaya Prakash et al (2005). Anandha Babu et al (2009, 2009a) had grown these crystals and studied their properties. Buyukgungor et al (2003) had reported the crystal structure of the donor–π–acceptor compound bis(2-aminopyridinium) maleate. However, no efforts were made to grow larger size crystals and their physico-chemical characterization analyses.

Many organic maleate crystals such as L-alaninium maleate (Natarajan et al 2006) and L-arginine maleate dihydrate (Sun et al 2008) are reported to be second harmonic generation active. Maleic acid, with relatively large π-conjugation, forms crystalline maleate of various organic molecules through hydrogen bonding and π–π interactions. It is known that maleic acid acts not only as an acceptor to form various π stacking complexes with other aromatic molecules but also as an acidic ligand to form salts through specific electrostatic or hydrogen bond interactions. In general, maleic acid can exist in neutral state as maleic acid or in ionized state as maleate. In the ionized state, it forms a very strong intramolecular hydrogen bond. Similarly, 2-aminopyridine molecules can exist in neutral form and protonated or cationic state. This chapter discusses the growth of D–π–A type single
crystals of bis(2-aminopyridinium) maleate (B2AM) from aqueous solution by slow evaporation technique and their characterization analyses.

2.3 SYNTHESIS OF B2AM

2-aminopyridine (C₅H₆N₂) and maleic acid (C₄H₄O₄) of analar grade were obtained from SRL, India. The compound was synthesized by dissolving 2-aminopyridine and maleic acid in the aqueous solution, in the ratio of 2:1. The precipitate of crystalline substance was obtained by continuous stirring. The identity of the synthesized material was confirmed by determination of the melting point using MONOTECH melting point apparatus. It shows that the material melts at 137 °C which fits to the results (Chitra et al 2008), it confirms that the synthesized material is bis(2-aminopyridinium) maleate. The chemical reaction may be represented as

\[ 2C_5H_6N_2 + C_4H_4O_4 \rightarrow 2C_5H_7N_2^+ . C_4H_2O_4^{2-} \]

In B2AM, maleic acid transfers two protons to 2-aminopyridine, thus the complex consists of 2-aminopyridine molecules in protonated form and maleic acid in doubly ionized state and the net positive charge resides on amino group. The synthesized compound was purified by successive recrystallization process and filtration.

2.4 SOLUBILITY AND METASTABLE ZONE WIDTH OF B2AM

The nucleation studies were carried out in a constant temperature bath (CTB) with cooling facility of accuracy of ±0.01 °C. The solubility at 30 °C was determined by dissolving the recrystallized salt of B2AM in 100 ml Millipore water of resistivity 18.2 MΩcm taken in an air tight container. The solution was stirred continuously for 6 h to achieve stabilization using an immersible magnetic stirrer. After attaining the
saturation, the concentration of the solute was estimated gravimetrically. The same procedure is repeated for different temperatures (35, 40, 45 and 50 °C). A graph of temperature dependence of solubility is depicted in Figure 2.1. It shows that B2AM has good solubility in water and it increases with temperature.

![Figure 2.1 Solubility curve of B2AM](image)

Metastable zone width is an essential parameter for the growth of large size crystals from solution, since it is the direct measure of the stability of the solution in its supersaturated region. The metastable zone width was measured by adopting the conventional polythermal method (Nyvlt et al 1970). The saturated solution (100 ml) at 30 °C was prepared according to the presently determined solubility data. After attaining the saturation, the solution was filtered by the filtration pump and Whatman filter paper of pore size 11 μm. The solution was preheated to 5 °C above the saturated temperature for homogenization and left at the superheated temperature for
about 1 h before cooling. Then it was slowly cooled at a desired cooling rate of 4 °C/h, until the first crystal appeared. The temperature was instantly recorded. The difference between the saturation temperature and nucleation temperature gives the metastable zone width of the system. Then experiment was repeated for different saturation temperatures 35, 40, 45 and 50 °C and the corresponding metastable zone widths were measured. Several runs (3–5 times) were carried out under controlled conditions for the confirmation of the saturation and nucleation points. The variation in solubility along with the metastable zone width for different temperatures is shown in Figure 2.2.

![Solubility and metastability curves of B2AM](image)

**Figure 2.2 Solubility and metastability curves of B2AM**

### 2.5 CRYSTAL GROWTH OF B2AM

The saturated solution of recrystallized salt of B2AM at room temperature of 35 °C was taken in a petridish with a perforated lid in order to control the evaporation rate, and kept for crystallization. The pH value of
aqueous solution was 5.9. The single crystals of B2AM were obtained after 20 days by slow evaporation method at room temperature. The photograph of the optically transparent B2AM crystals is shown in the Figure 2.3.

![Figure 2.3 Photograph of as–grown B2AM crystals](image)

**Figure 2.3 Photograph of as–grown B2AM crystals**

Morphology of the grown crystals was identified by the single crystal X-ray diffraction studies (Bruker Kappa APEXII). It establishes that the crystal has 8 developed faces out of which (001) and (00T) are prominent. For each face, its parallel Friedal plane is also present in the grown crystal and shown diagrammatically in Figure 2.4.
2.6 X-RAY DIFFRACTION STUDIES

The grown crystal was subjected to single crystal X-ray diffraction study using NONIUS CAD-4/MACH 3 diffractometer with MoKα radiation in the wavelength 0.71073 Å to identify the structure and to estimate the lattice parameter values. 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 2.1 in comparison with reported values (Buyukgungor et al 2003) and it shows that they are in close agreement. It is observed that the crystal belongs to the orthorhombic system with space group Fdd2.
Table 2.1 Crystal lattice parameters of B2AM

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Present study</th>
<th>Literature (Buyukgungor et al 2003)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>21.797 (3)</td>
<td>21.756 (5)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>23.556 (3)</td>
<td>23.531 (5)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>5.624 (2)</td>
<td>5.628 (11)</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>Volume (Å³)</td>
<td>2887.8 (2)</td>
<td>2881.2 (11)</td>
</tr>
<tr>
<td>System</td>
<td>Orthorhombic</td>
<td>Orthorhombic</td>
</tr>
</tbody>
</table>

Powder X-ray diffraction study was carried out 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 grown crystals were finely powdered and have been subjected to powder XRD analysis. The sample was scanned over the range 10–60° at the rate of 1°/min. The indexed powder X-ray diffraction pattern of B2AM is given in Figure 2.5. The well defined Bragg’s peaks at specific 2θ angles confirmed the crystallinity of B2AM.

![Figure 2.5 Powder XRD pattern of B2AM](image-url)
2.7 HIGH-RESOLUTION X-RAY DIFFRACTION (HRXRD) ANALYSIS

The crystalline perfection of the grown B2AM single crystal was characterized by HRXRD analysis by employing a multicrystal X-ray diffractometer designed and developed at National Physical Laboratory (Lal et al 1989). Figure 2.6 shows the schematic diagram of the multicrystal X-ray diffractometer. The divergence of the X-ray beam emerging from a fine focus X-ray tube (Philips X-ray Generator; 0.4 mm × 8 mm; 2kWMo) is first reduced by a long collimator fitted with a pair of fine slit assemblies. This collimated beam is diffracted twice by two Bonse-Hart (Bonse et al 1965) type of monochromator crystals and the thus diffracted beam contains well resolved MoKα₁ and MoKα₂ components. The MoKα₁ beam is isolated with the help of fine slit arrangement and allowed to further diffract from a third (111) Si monochromator crystal set in dispersive geometry (+, −, −). Due to dispersive configuration, though the lattice constant of the monochromator crystal and the specimen are different, the dispersion broadening in the diffraction curve of the specimen does not arise. Such an arrangement disperses the divergent part of the MoKα₁ beam away from the Bragg diffraction peak and thereby gives a good collimated and monochromatic MoKα₁ beam at the Bragg diffraction angle, which is used as incident or exploring beam for the specimen crystal. The dispersion phenomenon is well described by comparing the diffraction curves recorded in dispersive (+, −, −) and non-dispersive (+, −, +) configurations (Bhagavannarayana 1994). This arrangement improves the spectral purity (Δλ/λ << 10⁻³) of the MoKα₁ beam. The divergence of the exploring beam in the horizontal plane (plane of diffraction) was estimated to be << 3 arc s. The specimen occupies the fourth crystal stage in symmetrical Bragg geometry for diffraction in (+, −, −, +) configuration. The specimen can be rotated about a vertical axis, which is perpendicular to the plane of diffraction, with minimum angular interval of
0.4 arc s. The diffracted intensity is measured by using an in-house developed scintillation counter. To provide two-theta (2\(\theta_B\)) angular rotation to the detector (scintillation counter) corresponding to the Bragg diffraction angle (\(\theta_B\)), it is coupled to the radial arm of the goniometer of the specimen stage. 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. The detector was kept at the same angular position 2\(\theta_B\) with wide opening for its slit, the so-called \(\omega\) scan.

Figure 2.6 Schematic line diagram of multicrystal X-ray diffractometer designed, developed and fabricated at National Physical Laboratory

Before recording the diffraction curve to remove the non-crystallized solute atoms remained on the surface of the crystal 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 2.7 shows the high-resolution diffraction curve (DC) recorded for a typical B2AM single crystal specimen using (201) diffracting planes in symmetrical Bragg geometry by employing the multicrystal X-ray diffractometer with MoKα₁ radiation. The solid line (convoluted curve) is well fitted with the experimental points represented by the filled circles. On deconvolution of the diffraction curve, it is clear that the curve contains an additional peak, which is 11 arc s away from the main peak. This additional peak depicts an internal structural very low angle (tilt angle, α < 1 arc min) boundary (Bhagavannarayana et al 2005) whose tilt angle [misorientation angle, α (inset in the figure) between the two crystalline regions on both sides of the structural grain boundary] is 11 arc s from its adjoining region. FWHM (full width at half maximum) values for the main peak and the peak due to very low angle boundary are respectively 9 and 28 arc s. Though the specimen contain a very low angle boundary, the relatively low angular spread of around 100 arc s of the diffraction curve and the low FWHM values show that the crystalline perfection is reasonably good.

![Diffraction curve recorded for B2AM single crystal using (201) diffracting planes with MoKα₁ radiation](image-url)
The affect of very low angle boundaries may not be very significant in many device applications, but for applications like phase matching, it is better to know these minute details regarding crystalline perfection. Thermal fluctuations or mechanical disturbances during the growth process could be responsible for the observed low angle boundary. It may be mentioned here that such low angle boundaries could be detected with resolved peaks in the diffraction curve only because of the high-resolution of the multicrystal X-ray diffractometer used in the present studies.

2.8 FTIR SPECTRAL ANALYSIS

The FTIR spectrum of B2AM was recorded using Perkin-Elmer FTIR spectrum RXI spectrometer by KBr pellet technique in the range 400–4000 cm\(^{-1}\) at room temperature and the spectrum is shown in the Figure 2.8. In the spectrum, the band at 3426 cm\(^{-1}\) is due to the NH asymmetric stretching vibration of amino group. The bands at 2754 and 2475 cm\(^{-1}\) are assigned to the stretching vibrations due to the hydroxyl group of the maleic acid anion. Asymmetric and symmetric stretching of carboxylate group occurs at wavenumbers 1577 and 1381 cm\(^{-1}\) respectively. The band at 1678 cm\(^{-1}\) indicates C=N stretching. The in-plane and out-of-plane vibration modes of C–H group in 2-aminopyridine are identified at 1301 and 1161 cm\(^{-1}\) respectively. CCC in-plane bending vibrations and C–H in-plane vibrations are observed at 972 and 1060 cm\(^{-1}\) respectively. The absorption at 774 cm\(^{-1}\) indicates the aromatic ring in the compound. The peaks at 619 and 550 cm\(^{-1}\) are attributed the NH\(_2\) and C–N–C out-of-plane bending respectively. The frequency observed at 445 cm\(^{-1}\) is assigned to the C–NH\(_2\) in-plane bending in 2-aminopyridine.
2.9 THERMAL ANALYSIS

2.9.1 Thermogravimetric and Differential Thermal Analysis

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of B2AM were carried out simultaneously by employing TA instrument Model Q600 SDT thermal analyzer. The sample was heated at a rate of 10 °C/min in inert nitrogen atmosphere and the TGA–DTA curves are shown in the Figure 2.9. The DTA curve of B2AM shows an endothermic peak at 137 °C which can be attributed to the melting point of the sample. TGA trace reveals that weight loss of the sample starts from 105 °C and at 210 °C it shows complete weight loss. The shoulder peaks in DTA after the main peak at 137 °C corresponds to the decomposition of the material.
2.9.2 Differential Scanning Calorimetry

Thermal stability of B2AM crystal was further tested using differential scanning calorimetry (DSC) results. DSC study was performed by using TA instrument Model Q20 in the temperature range 25–300 °C at heating rate of 10 °C/min in inert nitrogen atmosphere. 3.4 mg of sample was placed in the Alumina crucible and DSC curve is depicted in Figure 2.10. DSC studies also show that B2AM melts at 137 °C and no phase transition was observed in this region which enhances the temperature range of the crystal for NLO applications.
2.10 DIELECTRIC STUDIES

The dielectric constant is one of the basic electrical properties of solids. Dielectric properties are correlated with the electro-optic property of the crystals (Aithal et al 1997). The capacitance \( C_{\text{crys}} \) and dielectric loss (\( \tan \delta \)) of B2AM crystal were measured using the conventional parallel plate capacitor method with the frequency range 100 Hz to 1 MHz using the Agilent 4284A LCR meter at various temperatures ranging from 313 to 353 K. A good quality crystal of size \( 5 \times 5 \times 2 \text{ mm}^3 \) was electroded on either side with graphite coating to make it behave like a parallel plate capacitor. The observations were made while cooling the sample and the air capacitance \( C_{\text{air}} \) was also measured.

The dielectric constant of the crystal was calculated using the relation

\[
\varepsilon_r = \frac{C_{\text{crys}}}{C_{\text{air}}} \tag{2.1}
\]
As the crystal area was smaller than the plate area of the cell, parallel capacitance of the portion of the cell not filled with the crystal was taken into account and, consequently the above equation becomes

$$\varepsilon_r = \frac{C_{\text{crys}} - C_{\text{air}} \left(1 - \frac{A_{\text{crys}}}{A_{\text{air}}} \right)}{C_{\text{air}}} \left(\frac{A_{\text{air}}}{A_{\text{crys}}}\right)$$

(2.2)

where $A_{\text{crys}}$ is the area of the crystal touching the electrode and $A_{\text{air}}$ is the area of the electrode.

Figure 2.11 shows the plot of dielectric constant versus applied frequency at different temperatures. The dielectric constant decreases with increasing frequency and finally it becomes almost a constant at higher frequencies for all temperatures. It is also indicates that the value of dielectric constant increases with increase in temperature. The same trend is observed in the case of variation of dielectric loss with frequency at different temperatures as shown in Figure 2.12. At 353 K, the dielectric constant of B2AM crystal at 100 Hz is 12.07, and this value decreases to 2.10 at 1 MHz. The electronic exchange of the number of ions in the crystals gives local displacement of electrons in the direction of the applied field, which in turn gives rise to polarization namely, electronic, ionic, dipolar and space charge polarization (Dharmaprakash et al 1989). Space charge polarization is generally active at lower frequencies and high temperatures and indicates the perfection of the crystal. As the frequency increases, a point will be reached where the space charge cannot sustain and comply with the external field and hence the polarization decreases, giving rise to decrease in values of dielectric constant. The characteristic of low dielectric constant and dielectric loss with high frequency for a given sample suggests that the sample possesses enhanced optical quality with lesser defects and this parameter is of vital importance for various nonlinear optical materials and their applications (Benet et al 1994).
Figure 2.11 Plot of dielectric constant versus applied frequency

Figure 2.12 Plot of dielectric loss versus applied frequency
2.11 UV–vis–NIR SPECTRAL STUDIES

The UV–vis–NIR spectrum of B2AM crystal was recorded with Lambda 35 spectrophotometer in the range 190–1100 nm and the recorded spectrum is shown in the Figure 2.13. The cutoff wavelength of B2AM crystal is 354 nm. The recorded spectrum shows that crystal has wide transmission of above 50% up to 1100 nm.

![Transmittance spectrum of B2AM crystal](image)

**Figure 2.13 Transmittance spectrum of B2AM crystal**

2.12 NLO PROPERTY

Powder SHG test offers the possibility of assessing the nonlinearity of new materials. Kurtz and Perry (1968) proposed a powder SHG method for comprehensive analysis of the second order nonlinearity. This is an important method for characterizing the materials before going through the long and tedious process of growing large optical quality crystals. The nonlinear
optical property of B2AM was confirmed, and the SHG efficiency in the powdered form was measured by the Kurtz and Perry powder method. A Q-switched Nd: YAG laser (DCR11) was used as light source. A laser beam of fundamental wavelength 1064 nm, 8 ns pulse width, with 10 Hz pulse rate was made to fall normally on the sample cell. The power of the incident beam was measured using a power meter. The transmitted fundamental wave was passed over a monochromator (Czemy Turner monochromator), which separates 532 nm (second harmonic signal) from 1064 nm, and absorbed by a CuSO$_4$ solution, which removes the 1064 nm light, and passed through BG34 filter to remove the residual 1064 nm light and an interference filter with bandwidth of 4 nm and central wavelength of 532 nm. The green light was collected by a photomultiplier tube (Hamamatsu). Potassium dihydrogen phosphate (KDP) crystal was powdered and was used as reference material in the SHG measurement. The input laser energy incident on the powdered sample was chosen to be 11.5 mJ/pulse. The B2AM second harmonic signal of 210 mV was obtained, while the KDP gave SHG signal of 50 mV for the same input beam energy. Thus SHG relative efficiency of B2AM was found to be 4.2 times that of KDP.

The comparison of melting point, cutoff wavelength and relative SHG efficiency of B2AM with other maleate crystals are depicted in Table 2.2. It strongly suggests that B2AM is a potential candidate for SHG applications compared to other maleate crystals.
Table 2.2 Melting point, cutoff wavelength and relative SHG efficiency of maleate crystals

<table>
<thead>
<tr>
<th>Name of crystal</th>
<th>Melting point (°C)</th>
<th>Cutoff wavelength (nm)</th>
<th>SHG (KDP = 1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-alaninium maleate (Natarajan et al 2006)</td>
<td>162</td>
<td>310</td>
<td>1.5</td>
</tr>
<tr>
<td>L-arginine maleate dihydrate (Mallik et al 2005, Sun et al 2008)</td>
<td>99</td>
<td>300</td>
<td>3</td>
</tr>
<tr>
<td>Bisglycine maleate (Balasubramanian et al 2010)</td>
<td>179</td>
<td>330</td>
<td>0.8</td>
</tr>
<tr>
<td>L-phenylalaninium maleate (Anbucezhiyan et al 2009)</td>
<td>160</td>
<td>240</td>
<td>0.27</td>
</tr>
<tr>
<td>L-arginine formomaleate (Mallik et al 2007)</td>
<td>137</td>
<td>315</td>
<td>1.2</td>
</tr>
<tr>
<td>2-aminopyridinium maleate (Anandha babu et al 2009)</td>
<td>148</td>
<td>350</td>
<td>3.5</td>
</tr>
<tr>
<td>B2AM (Present work)</td>
<td>137</td>
<td>354</td>
<td>4.2</td>
</tr>
</tbody>
</table>

2.13 MECHANICAL STUDIES

Mechanical strength of the materials play a key role in the device fabrication. Vickers hardness is one of the important deciding factors in selecting the processing (cutting, grinding and polishing) steps of bulk crystal in fabrication of devices based on crystals. Vickers microhardness measurements on (001) plane of B2AM crystals were done by using Shimadzu HMV-2 hardness tester at room temperature. The Vickers microhardness number, \( H_V \) was calculated using the relation (Mott 1956):

\[
H_V = 1.8544 \left( \frac{p}{d^2} \right) \text{ kg/mm}^2
\]  

(2.3)
where \( p \) is the applied load (g) and \( d \) is the diagonal length (\( \mu \text{m} \)) of the indentation. The indentation time was kept at 10 s and microhardness value was taken as the average of the several impressions made. Figure 2.14 shows the variation of \( H_V \) as function of applied load ranging from 20 to 100 g on B2AM crystal.

![Figure 2.14 Plot of dependence of Vickers microhardness number on load](image)

It is clear from the figure that \( H_V \) increases with an increase of the load. The value of \( H_V \) at 20 g is 18.16 kg/mm\(^2\) and it increases to 37.33 kg/mm\(^2\) at 100 g. This type of behavior wherein the hardness number increases with increasing applied load is called reverse indentation size effect (Sangwal et al 2002).

2.14 CONCLUSIONS

The bulk size single crystals of B2AM were grown by slow evaporation technique. Single crystal X-ray diffraction studies reveal that B2AM crystallizes in orthorhombic system with space group Fdd2. Morphology of the as–grown crystal was identified. The solubility and metastable zone width of the material were determined for water solvent.
HRXRD analysis shows that the crystalline perfection of the as–grown crystal is reasonably good. The FTIR analysis confirms the presence of functional groups in the grown crystals. Dielectric studies show that B2AM has low values of dielectric constant and dielectric loss at high frequencies. The melting point of B2AM at 137 °C was identified from thermal studies. Optical spectrum reveals that B2AM crystal has good transmission window with UV cutoff wavelength at 354 nm. The SHG relative efficiency of B2AM was found to be 4.2 times that of KDP.