CHAPTER 2

GROWTH OF 3-NITROACETANILIDE SINGLE CRYSTAL
BY VERTICAL BRIDGMAN TECHNIQUE AND ITS
CHARACTERIZATION

2.1 INTRODUCTION

Since the advent of lasers, there has been an explosion in the
discovery of nonlinear optical effects in materials. The nonlinear response of
a material to the applied optical field is being widely used by the scientific
community in practical device applications. An optical nonlinearity can result
in harmonic light generation, transient grating formation and excitation of
lattice or molecular vibrations. Advanced laser based imaging,
communication, data storage and countermeasure system designs require
improved nonlinear optical (NLO) materials. In particular, there are
identifiable systems applications for lower-cost, higher response, higher
average power NLO materials for optical parametric operation and second
harmonic generation (SHG) throughout the blue/near UV spectral region.
Ever since the discovery of nonlinear optical properties in organic crystals,
the search in these new materials which possess sufficiently large nonlinear
coefficient, ultraviolet generation and ease of growing large size bulk single
crystals is in progress.

In this chapter the growth and characterization of organic molecular
NLO crystal 3-nitroacetanilide (mNAA) from melt by Bridgman technique is
reported. The mNAA also known as N-(3-nitrophenyl) acetamide, C₈H₆N₂O₃,
is an organic non-linear optical material. It crystallizes in the monoclinic system in the chiral space group P2\(_1\), and there are four independent molecules in the asymmetric unit. Figure 2.1 shows the molecular structure of mNAA.

The 3-nitroacetanilide compound is found to be of interest as an organic non-linear optical (NLO) material. The crystals show optical second harmonic generation with the fundamental beam (\(\lambda = 1064 \text{ nm}\)) of Nd:YAG laser. The single-crystal structure elucidation further reinforces this observation.

![Figure 2.1 Molecular structure of mNAA](image)

Figure 2.2 shows the asymmetric unit of the title compound. The torsion angles about the C(phenyl)-N(amide) and C(phenyl)-N(nitro) bonds show that the amide and nitro groups lie in the plane of the phenyl ring. The carbonyl group is involved in hydrogen bonding, unlike the case of 2-nitroacetanilide (Kashino et al 1986). The packing in Figure 2.1 is stabilized by N-H---O and C-H---O hydrogen bonds. H atoms were positioned geometrically and allowed to ride on their respective parent atoms; C-H = 0.93 ± 0.96 Å, and \(U_{\text{iso}} = 1.2U_{\text{eq}}\)(NH and ring CH) or 1.5\(U_{\text{eq}}\)(CH\(_3\) and CH\(_2\)).
MATERIAL SYNTHESIS

The m-nitroacetanilide compound was synthesized from the analytical reagent (AR) m-Nitroaniline (m.NA) and acetic anhydride (AA) obtained from SRL company without further purification. The compound was prepared by mixing of m.NA and acetic anhydride in equimolar ratio (1:1), dissolved in 100 ml of methanol at room temperature. The whole solution was taken in a round-bottomed flask fitted with water-cooled condenser. K$_2$CO$_3$ was added to speed up the reaction. The mixture was refluxed for about 6 h. The refluxed solution was cooled to room temperature and the precipitated mNAA was separated by vacuum filtration. The yellow colored precipitate was washed with deionized water. The precipitate was subjected to recrystallization in order to remove the impurities present in the compound. The solution was prepared by using the recrystallized salt and stirred well with the help of magnetic stirrer for 60 minutes. The prepared solution was kept in a petridish for the evaporation of the solvent. Yellow colour single crystals of mNAA were obtained from the recrystallized salt from slow
evaporation solution growth technique. The melting point of the grown crystals was found using melting point apparatus and the material was found to melt at $\approx 160$ °C.

Though the mNAA crystals were obtained from solution growth technique, the crystals were not good in quality and much smaller in size, of the order of $3 \text{ mm} \times 2 \text{ mm} \times 2 \text{ mm}^3$. In order to grow larger size mNAA single crystal with transparency and good quality, the melt growth technique was chosen. Prior to the growth, the compound was subjected to thermal analysis such as differential thermal analysis/thermogravimetric analysis (DTA/TGA) differential thermal analysis (TG/ DTA) to determine the thermal stability of the material. The thermal analysis of the compound is discussed later. It was found that the synthesized compound is thermally stable with congruent melting point. From the result it was observed that mNAA can be grown by melt growth technique.

2.3 MELT GROWTH

Growth of organic crystals from the vapour phase usually results in slow growth of very thin crystal (Karl 1980; Buckley 1951). Thus, when large single crystals are required, these must be grown from the melt (Kannan et al 2006), or from saturated solution (Meera et al 2002).

The lower melting point of the organic crystals often offers the advantage that transparent glass-made growth apparatuses can be used, in which the growth process can be easily followed by direct observation. There are many uses for transparent furnaces in materials processing and fluid and solid mechanics at elevated temperatures. Transparent furnaces can be used for research in crystal growth, sintering, metal joining, and annealing, high temperature materials properties, and the behavior of flowing systems that use
high temperature liquids. In the area of crystal growth, some of the capabilities introduced by a transparent furnace are: 1) Nucleation can be observed; if multiple nucleation sites occur solidification can be restarted, 2) The melt/solid interface can be viewed as a result of differences in density and emissivity between the liquid and solid, 3) Surface tension effects can be studied as a result of these liquid-solid differences, 4) Convection can be studied through index of refraction changes with temperature, 5) Internal temperatures can be monitored by tomographic means, and 6) A variety of crystal defects are visible, depending on the optical properties of the crystal (Stephen et al 1997).

2.4 CONSTRUCTION OF FURNACE

A glass tube was used for Bridgman furnace; the furnace separated into two zones, each 30 cm long. Each zone was wound with thin Al Kanthal of thickness 0.5 mm having total resistance of 50 ohms. For winding, ceramic thread has been used for grip in the glass material. The space between the winding was kept as 2 mm. The setup was enclosed by a concentric borosilicate glass tube, which ensured the thermal insulation. The schematic diagram of the vertical growth furnace with translation setup is shown in Figure 2.3.

The setup has been enclosed by a black envelope to provide light shielding for the material during growth because of photo plastic nature (Kojima 1981) and dimerisation of the grown crystals is possible due to UV-Visible light exposure at high temperatures. The growth furnace was placed on the wooden stool whose bases are supported by vinyl sheets to avoid vibration and the stool was leveled using spirit level so that the furnace had no asymmetric tilt. With this arrangement and by virtue of the heavy weight of the furnace itself mechanical vibration was practically eliminated. The
temperature of the furnace was controlled by programmable Eurotherm PID controllers.

Figure 2.3 Schematic diagram of the transparent Bridgman-Stockbarger setup

The photograph of the two zone glass furnace is shown in Figure 2.4.
Because there is no forced convection in the melt during Bridgman growth, a slower growth rate should be used to grow the crystals with higher quality. The rate of crystal growth sets an upper limit to the rate at which the crystal-growing vessel can be lowered in the oven. A rate of 1-2 mm/h has been recommended as an upper limit for organic crystals, in contrast to 20 mm/min for metals and 1-4 mm/h for ionic crystals (Sherwood 1960). The larger diameter crystals should be grown by even slower growth rate. However the reports proposed a constant growth rate for full growth of crystals. But the organic crystals are of low thermal conductivity. So, if the diameter of the ampoule increases the translation rate must be reduced.
A translation assembly has been developed using a DC motor with multistage gear setup. A conical screw type mechanism (Figure 2.3) was used to translate the ampoule. The screw was fixed to the end of the gear setup. One end of a Teflon thread was rolled in the conical type screw and the other end was fixed on the ampoule via metal wire and two pulleys. The thread was rolled towards the bigger diameter from the end of the screw. A 2 cm long cylindrical rod has been fixed at the end of the conical screw. When the DC motor rotates with a constant speed, the translation smoothly decreases as the diameter of the screw decreases there after the translation was at a constant rate.

2.6  PURIFICATION PROCESSES

The commercially purchased material contains impurities. Before crystal growth the purification is important. In this work the following purification procedures were involved.

2.6.1  Recrystallisation from Solvent

This process involves identifying a suitable solvent in which the material to be recrystallised or purified has high solubility at elevated temperature (typically near the boiling point of the solvent) and low solubility at low temperature. The solid (or mixture) is dissolved in a minimal volume of hot solvent, filtered to remove any insoluble components in the mixture and the solution is slowly cooled to allow the product to crystallise. The formation and growth of crystals is a complex process that involves the removal of molecules from solution (molecule by molecule) and stacking them into a regular condensed state where the molecules are packed in a crystal lattice. Like molecules tend to pack more efficiently, so the growth of crystals tends to bring together molecules of the same type. The effect of dissolving a solid in a solvent and then permitting it to crystallise is that the
crystals that form contain less impurities than the material that was originally dissolved. Successive recrystallisations can produce extremely pure crystalline samples.

2.6.2 Zone Refining

The zone refinement process has been used successfully to remove impurities that are generally not removable by other purification methods. A furnace designated for zone refinement processing has been designed and built. The furnace consists of three asbestos cement sheets A, B and C (Figure 2.5) of thickness 0.5 cm and radius 15 cm. The asbestos cement sheets A and C have holes at the centre, slightly greater than the diameter of the tube in which the zone refining is to be carried out. The diameter of the hole in the central asbestos sheet B is about 2 mm more than that of A and C. The heating coil is wound on B (Figure 2.5). An ordinary Kanthal heating element is used as a heating coil. The closed electric connections were taken out through a twin bore ceramic tube. The three asbestos cement sheets along with the heating coil and thermocouple were fixed by screws and nuts, and were kept in a stand. This furnace provided temperature of up to 350°C with a heating zone of about 1.5 cm. A sample to be purified is sealed in an ampoule. A small, evacuated, and sealed ampoule (filled with material to be purified) is then pulled upward along the length of the furnace by a motor at a pre-determined speed. This was repeated many times. The purified materials were collected and filled in another ampoule. Then the ampoule traversed downward direction and it was repeated many times. Impurities migrate away from the melted region, which slowly pushes the impurities to the ends of the entire material sample.
2.7 CRYSTAL GROWTH OF m-NITROACETANILIDE

The bulky single crystals of mNAA were grown using the Bridgman crystal growth technique. The material was purified by sublimation and zone-refining techniques. For the sublimation process, a Pyrex combination assembly tube was used and evacuated to a residual pressure of $10^{-3}$ torr (1 torr $= 133.322$ Pa).

For zone refining, 15, 17 zones were passed down through a 130 mm long column of the material. This took about 240 h. The temperature of the heater was adjusted to obtain the melting point of mNAA which falls in the range $\sim 156$-$160$ °C. The whole process of zone refining was repeated until no black impurities were detected.
The single crystals of mNAA were grown using a growth setup mentioned above. The optimum condition of mNAA growth in the preliminary trials was a steep temperature gradient with upper and lower ends of the furnace at ~170 and 140 °C respectively. The temperature was uniform over 20 mm length above and below the ends of the heating elements.

The zone refined mNAA was then put in the borosilicate glass ampoule in which the capillary was placed at the bottom. The inner diameter of the ampoule was 18 mm. The ampoule was sealed after it was evacuated to $10^{-4}$ torr and the Bridgman growth was employed. The growth ampoule was placed at the constant temperature region of the furnace. The temperature was raised slowly until the material was completely melted. The rate of lowering the crystal growth tube was 1 mm h$^{-1}$. Continuous lowering through the temperature gradient resulted in crystal growth. The lowering rate for organic materials is usually on the lower side due to their slow growth rate and low thermal conductivity. When all the melt in the crystal growth tube had changed to a crystal, the lowering motor was switched off. The furnace was initially cooled at 1 °C/h from the set temperature for 5 °C in order to avoid cracks due to the difference in thermal expansion coefficient between the glass and crystal. The ampoule was slowly cooled to room temperature over a period of 3 days. After crystal growth was completed, the crystal was removed from the growth ampoule by carefully cutting the ampoule into two halves vertically using a standard diamond wheel cutter. Finally, a yellow colored transparent single crystal of 30 mm length and 18 mm diameter was obtained. The crystal is shown in Figure 2.6 (a). 5mm cleaved ingot of mNAA is shown in Figure 2.6 (b).
Figure 2.6(a) As grown single crystal of mNAA from Bridgman technique

Figure 2.6 (b) Cut and cleaved ingot of mNAA crystal
2.8 X-RAY DIFFRACTION (XRD) ANALYSIS

The melt grown crystal of mNAA was subjected to single crystal XRD and powder XRD analysis. The single crystal XRD reveals that the mNAA crystal belongs to monoclinic system. The space group is P2₁ and the cell parameters are: \( a = 9.767\,\text{Å}, b = 13.298\,\text{Å}, c = 13.272\,\text{Å}, \beta = 102.991^\circ, \) \( V = 1679.8\,\text{Å}^3. \) The obtained cell parameters are in good agreement with earlier report (Mahalakshmi et al 2002). The powder XRD pattern of the crystal was recorded with a SIEFERT X-ray diffractometer using CuKα radiation \( (\lambda = 1.5418\,\text{Å}) . \) The sample was scanned using a \( 2\theta \) range of \( 10 - 70^\circ \) at a scan rate of 1°/min. The powder XRD pattern of mNAA is shown in Figure 2.7. The calculated \( (h, k, l) \) planes satisfy the general reflection conditions of space group observed from the structure determination of the crystal. The \( (h, k, l) \) planes were indexed with the help of the DICVOL91 program.

![Figure 2.7 Powder X-ray diffraction pattern of mNAA crystal](image-url)
2.9 **FOURIER TRANSFORM INFRARED (FT-IR) SPECTRAL ANALYSIS**

Infrared spectra are an important record, which provide more information about the structure of a compound. In this technique almost all functional groups in a molecule absorb characteristically within a definite range of frequency (Kalsi 1985). The absorption of IR radiation causes the various bands in a molecule to stretch and bend with respect to one another. The most important range (4000-400 cm\(^{-1}\)) is of prime importance for the study of an organic compound by spectral analysis (Dyer 1987). In the present study, the FT-IR spectrum was recorded in the range 4000-400 cm\(^{-1}\) for the mNAA single crystal using the KBr pellet technique. Figure 2.8 shows the FT-IR spectrum of mNAA. The characteristic absorption bands were observed in spectral range 500–1800 cm\(^{-1}\). In the mNAA molecular-packing diagram proposed by Mahalakshmi et al (2002), there is a formation of hydrogen bond between C-H of the aromatic ring and O of the carbonyl group and C-H and O of NO\(_2\) group.

![Figure 2.8 FT-IR spectrum of mNAA crystal](image-url)
In the FT-IR spectrum the peak due to aromatic C–H stretching appears as a weak absorption band at 3263 cm$^{-1}$ and hence the hydrogen-bonding interactions could be strong. The N-H plane bending modes are positional at 1600 cm$^{-1}$. The medium absorption bands at 1529 and 1350 cm$^{-1}$ are attributed to N=O (aromatic NO$_2$) asymmetric stretching and N=O (aromatic NO$_2$) symmetric stretching vibrations respectively, which indicate that the carbonyl oxygen atoms are more active as hydrogen bond acceptors than the nitro-oxygen atom. The bands assigned to C–C stretching vibrations are weaker and appear in the broader region of 1200–800 cm$^{-1}$. The absorption band at 740 cm$^{-1}$ was assigned to the out of plane =C–H bending in the FT-IR spectrum.

2.10 LASER RAMAN SPECTRAL ANALYSIS

Figure 2.9 shows the Raman spectrum of mNAA crystal. The sharp intense band in infrared spectrum at 1674 cm$^{-1}$ is assigned to C=O stretching mode, which is also observed in Raman spectrum at 1694 cm$^{-1}$ as a medium intense band. The NH in plane bending mode is coupled with ring modes of carbonyl, among which the mixing of NH in plane bending with C=O mode enhances the band intensity. The C–N stretches can be found in the region 1358 cm$^{-1}$, mixed with the aromatic CH in plane bending modes and the NH out of plane bending modes are coupled with the CH out of plane bending in the region 874–742 cm$^{-1}$. The C–C/C–N stretches can be observed as a strong band at 1245 cm$^{-1}$ in Raman. The C–C stretching mode is influenced by hyperconjugation and C–N stretch is influenced by increased bond order due to donor–acceptor interaction, both of which have frequency increasing tendency. Since these modes correspond to mixed vibrations, the relative weightage of the above two influences remain unpredictable. The peak at 854 cm$^{-1}$ corresponds to the aromatic C-H bending vibrations, which occur
due to interaction of C=O wags. The OCH₃ groups can be confirmed with the peak at 1123 cm⁻¹. (CO)CH₃ peak in mNAA is observed at 1694 cm⁻¹.

![Raman Spectrum of mNAA crystal](image)

**Figure 2.9 Raman Spectrum of mNAA crystal**

The band at 1750 cm⁻¹ is due the presence of NO₂ of mNAA in the Raman spectrum.

### 2.11 UV-Vis-NIR SPECTRAL ANALYSIS

The transparency of mNAA crystal is shown in Figure 2.10. The transmittance spectra of NLO material play a major role in device fabrication. Wider the transparency window more will be the practical applicability of that material. The transmission curve of conventional grown and the melt grown mNAA crystal was measured by using a UV visible spectrometer SHIMADZU-1601) UV-Vis-NIR recording spectrophotometer in the wavelength range 200 to 1200 nm. The thickness of the crystal slice used in the experiment is 1 mm. From the figure it is observed that the UV
transparency cutoff occurs at 400 nm. Further, there is no undesirable absorption in the spectra and the transmission is greater than 50% which is good enough for the harmonic generation using a diode laser.

![Transmission spectrum of mNAA crystal](image)

**Figure 2.10 UV-Vis-NIR spectrum of mNAA crystal**

### 2.12 POWDER SHG MEASUREMENT

A second harmonic conversion experiment was carried out for the mNAA crystals. A Q-switched YAG laser operating at 1.06 µm with a pulse length of 10 ns was used to investigate the frequency doubling (SHG) and to evaluate the crystal quality. The synthesis of the title compound has been undertaken in order to obtain a material with strong second harmonic generation properties. However, the nonlinear optical properties of mNAA were found to be rather weak in comparison to urea and it is 1.2 times greater than that of the KDP.
2.13 THERMAL STUDIES

2.13.1 Differential Thermal Analysis/Thermogravimetric Analysis (DTA/TGA)

Thermal properties of the material were studied by thermogravimetric (TGA) and differential thermal analyses (DTA). The TGA was carried out between room temperature and 600 °C in the nitrogen atmosphere at a heating rate of 10K/min and the spectrum is shown in Figure 2.11. The material exhibits single sharp weight loss starting at 300 °C and below this temperature no significant weight loss is observed. Hence the compound is stable up to 300 °C. This type of weight loss illustrates volatilization rather than degradation.

In order to confirm melting and subsequent volatilization of this material without decomposition, DTA analysis was undertaken. The analysis was also carried out between room temperature and 600 °C in the nitrogen atmosphere at a heating rate of 10K/min and the resulting spectrum is shown in Figure 2.12.
There is a sharp endotherm at 154 °C, which is assigned to melting. Below this endotherm there is no exothermic or endothermic peak. This confirms the absence of any isomorphic transition. After melting, no characteristic exothermic or endothermic peaks were observed up to 380 °C which indicates that there is no degradation of the compound above the melting point. Sharpness of the endothermic peaks observed in DTA indicates good degree of crystallinity of the sample.

![DTA trace of mNAA crystal](image)

**Figure 2.12 DTA trace of mNAA crystal**

### 2.13.2 Differential Scanning Calorimetric (DSC) Analysis

The thermal property of mNAA was further confirmed by using NETZSCH DSC 204 Differential Scanning Calorimetry (DSC) with a heating rate of 10.0 K/min in the nitrogen atmosphere. A small piece of crystal weighing 15.630 mg was placed in an aluminum pan. The pan was encapsulated with dome lid, which was crimped in position. The DSC of the grown crystal is shown in Figure 2.13. At 161°C a sharp peak is observed which represents its melting point. The sharpness of this peak shows good degree of crystallinity of the sample. There are no additional peaks observed
after its melting. The melting point was also measured directly using TEMPO melting point apparatus which yielded as 159 °C.

![Figure 2.13 DSC curve of m-NAA crystal](image)

**Figure 2.13 DSC curve of m-NAA crystal**

### 2.14 DIELECTRIC STUDIES

Figure 2.14 (a) shows the plot of dielectric constant ($\varepsilon_r$) versus applied frequency. The dielectric constant has high value in the lower frequency region and then it decreases with the applied frequency. The characteristic of low 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 NLO materials in their application (Balarew and Duhlew 1984). Figure 2.14 (b) shows the plot of dielectric loss ($\varepsilon_l$) versus applied frequency.
Figure 2.14 (a) Variation of dielectric constant of mNAA crystal with frequency (b) Variation of dielectric loss with frequency of mNAA crystal
2.15 CONCLUSION

Single crystal of mNAA has been grown by Bridgman technique up to 30 mm length and 18 mm diameter. The functional groups have been confirmed by FTIR analysis. From the thermogravimetric analysis it was found that the material exhibits single sharp weight loss starting at 300 °C which indicates that the material is thermally stable. And from DTA, it is seen that the material has a sharp endotherm at 154 °C, which is assigned to melting and there is no exothermic or endothermic peak observed below the melting point. The optical behaviour has been studied using UV–vis analysis and found that there is no absorption between 400 and 1200 nm, which is the key requirement for NLO materials. The SHG efficiency of mNAA was found to be 1.2 times higher than that of KDP. Dielectric studies of mNAA shows that both dielectric constant and loss of the crystal decrease with increase in frequency.