X-ray diffraction, spectroscopic and mechanical studies on potential organic NLO materials of metaNitroaniline and N-3-Nitrophenyl Acetamide single crystals

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Abstract. In the present paper, attempts were made to grow good quality metaNitroaniline (mNA) and N-3-Nitrophenyl (3-NAA) single crystals. The lattice parameter values from the Powder X-ray diffraction pattern confirms that mNA belongs to orthorhombic crystal system with the unit cell parameter values of \(a = 6.501 \, \text{Å}, \quad b = 19.330 \, \text{Å}, \quad \text{and} \quad c = 5.082 \, \text{Å}\) with space group \(Pbc_2_1\). Similarly the powder XRD data indicates that 3-NAA crystal retained its monoclinic structure with lattice parameter values \(a = 9.762 \, \text{Å}, \quad b =13.287 \, \text{Å}, \quad \text{c} =13.226 \, \text{Å}, \quad \text{and} \quad \beta = 102.99^\circ\). Investigation has been carried out to assign the vibrational frequencies of the grown crystals by Fourier Transform infrared spectroscopy technique. The SHG efficiency of mNA and 3NAA was determined by Kurtz and Perry powder technique. The Optical absorption study confirms the suitability of the crystals for device applications. The mechanical properties of the grown crystals have been studied using Vickers microhardness tester.

1. Introduction
The emergence of new materials with superior quality is often responsible for major advances in new technologies. In that respect, materials with a nonlinear optical response are expected to play a major role in enabling optoelectronic and photonic technologies [1]. Materials with large nonlinear optical susceptibilities are of current interest in the area of harmonic generation and optical modulation. In recent years, some polar organic crystals, which form a non-centrosymmetric structure exhibit second-order nonlinear optical properties that far surpassed those of the conventional materials [2]. Organic molecules with significant nonlinear optical activity generally consist of a \(\pi\) – electron conjugated structure. The conjugation \(\pi\) -electron moiety provides a pathway for the entire length of conjugation under the perturbation of an external electric field. Fictionalization of both ends of the \(\pi\) bond systems with appropriate electron donor and acceptor group can increase the asymmetric electronic distribution in either or both the ground and excited states, thus leading to an increased optical nonlinearity [3].

2. Synthesis Solubility and Growth of mNA and 3NAA Single Crystal
The purified mNA material was used for solubility studies and to grow bulk single crystal. Since mNA is less soluble in water, acetone was chosen as the solvent. The selected solvent and an excess amount of mNA were added to a 250 ml glass container. The solution was gently stirred for an optimum period to attain saturation. The solution was saturated at 40 \(^\circ\)C and the crystals were grown. The habits of the
grown crystals were pyramidal in shape. The 3NAA compound was synthesized by the direct combination of N-(3-nitrophenyl) acetamide and acetic anhydride in methanol at room temperature. According to the solubility curve, the saturated solution of 3NAA was prepared by dissolving the source material in the mixed solvent of acetone and methanol (1:1). On reaching saturation, the beaker containing the growth solution was optimally closed for controlled evaporation. Transparent single crystals were obtained from the growth solution after 10 days.

3. Characterization

3.1 Powder X-ray diffraction studies
Finely crushed powder of mNA and 3NAA crystals were subjected to powder X-ray diffraction analysis using CuKα (λ = 1.5418 Å) radiation. The sample was scanned at a scan rate of 2 degree/minute. The recorded X-ray diffraction pattern of mNA and 3NAA are shown in figure 1 and 2. It is confirmed that mNA belongs to orthorhombic crystal system, the unit cell parameters were found to be a = 6.501 Å, b = 19.330 Å, and c = 5.082 Å with point group mm2, space group Pbc21 and Z = 4. Using the simulated hkl values and the experimental d values, the lattice parameters were estimated and this indicates that 3NAA crystal retained its monoclinic structure with lattice parameters values a = 9.762 Å, b = 13.287 Å, c = 13.226 Å, and β = 102.99°. The results were in good agreement with the reported values [4, 5].

![Figure 1. Powder X-ray diffraction pattern of mNA](image1)

![Figure 2. Powder X-ray diffraction pattern of 3NAA](image2)

3.2 FT-IR spectral analysis
The mNA sample was prepared by mixing powdered mNA with potassium bromide and a pellet was made. The FT-IR spectrum obtained for mNA sample is shown in Figure 3. Symmetric and asymmetric stretching modes of free NH₂ group are observed at 3328 and 3430 cm⁻¹. The peaks at 3201, 3094 and 2923 cm⁻¹ are due to very weakly bonded N–H stretching modes. The peaks at 2359 cm⁻¹ may be assigned to overtone of bands at 1264 and 1087 cm⁻¹. The NH₂ band is observed at 1623 cm⁻¹. The peaks that appear at 1520 and 1348 cm⁻¹ are due to the vibrations of NO₂ stretching modes. As either the N–H stretching modes or the NO₂ stretching modes are not much broad, their interaction with the neighboring molecules was presumed to be weak bonds. The vibrations between 909 and 650 cm⁻¹ are usually associated with the presence of benzene rings in the mNA molecule. The peaks between 750 and 810 cm⁻¹ show the meta position of the substituted molecules in the benzene ring of mNA.
The FT-IR spectrum was recorded on the grown 3-NAA crystal at room temperature in the range of 500 – 4000 cm\(^{-1}\) and is shown in the figure 4. The spectrum shows the symmetric and asymmetric stretching modes of free NH\(_2\) group, which are observed at 3303 and 3263 cm\(^{-1}\). The absorptions at 1673 cm\(^{-1}\) are due to ketone stretching vibration. The aromatic skeletal ring is observed at 1600 cm\(^{-1}\). A well-resolved peak at 604 cm\(^{-1}\) represents the C-N-O stretching vibration. Peak at 1260 cm\(^{-1}\) is due to N-H bending and C-N stretching vibrations. The vibration observed between 886 and 670 cm\(^{-1}\) are usually associated with the presence of benzene rings in the 3NAA molecule. The peak between 741 and 805 cm\(^{-1}\) shows the meta position of the substituted molecule (NO\(_2\)) in the benzene ring of 3NAA. The peaks at 1531 and 1350 cm\(^{-1}\) are due to the vibration of NO\(_2\) stretching modes. As either the N-H stretching modes or NO\(_2\) stretching modes are not much broad, their interaction with the neighboring molecule is presumed to be weak bonds.

### 3.3 Optical assessment

Optical absorption spectra were recorded and the recorded spectra are shown in Figure 5 and Figure 6. From the spectra, it is seen that the mNA crystal has a lower cut-off wavelength of 240 nm. The UV–Vis–NIR spectrum gives limited information about the structure of the molecule because the absorption of UV and visible light involves the promotion of the electron in s and p orbitals from the ground state to higher energy states. It can be seen that 3NAA is transparent in the range 270 – 1200 nm and is the required important property in nonlinear optical applications. The wide transparency in the visible region is one of the additional key requirements for having efficient NLO character [6].

### 3.4 Second harmonic generation efficiency measurement

The SHG efficiency was estimated using Kurtz and Perry technique [7]. SHG was confirmed by the emission of green light. Using the potassium dihydrogen phosphate (KDP) crystalline powder as reference material, the output of SHG signal was compared and found that the SHG conversion efficiency of mNA is 28 times and 3-NAA is 4 times that of KDP.
3.5 Vickers microhardness studies

Microhardness studies were carried out on mNA and 3-NAA single crystals using Vickers hardness tester fitted with pyramidal indentor. The diagonal length of the indentation in mm for various applied loads in kg is measured for a constant indentation time of 15 s. The Vickers hardness number is calculated using the relation $H_v = \frac{1.8544p}{d^2}$ kg/mm$^2$. According to Onitsch for $1.0 \leq n \leq 1.6$, the material is regarded as hard material and $n > 1.6$ for soft materials [8]. For mNA and 3-NAA, $n$ is found to be greater than 1.6, thus confirming that both the crystals are soft materials.

4. Conclusion

The title compounds of mNA and 3-NAA were successfully synthesized and the single crystals have been grown by solution growth technique. Its cell parameters have been determined by the powder XRD analysis. The presence of functional groups has been identified from the FTIR analysis. Optical absorption study reveals the transparency of the grown crystals. Second harmonic efficiency of the grown crystals has been confirmed by Kurtz and Perry powder method. The microhardness measurements prove that both belongs to the soft category of materials.

5. References

[1]. Sankar, D, Praveen Kumar. P, Madhavan J, Physica B, 405(2010) 1233.
[2]. T. Sujatha , A. Cyrac Peter , M. Vimalan , J. Merline Shyla , J. Madhavan, Physica B, 405(2010)3365
[3]. J. Madhavan, S. Aruna , A. Anuradha, D. Premanand, I. Vetha potheher ,K. Thamizharasan , P. Sagayaraj, Optical Materials, 29(2007A) 1211
[4]. Senthil. S, Pari. S, Sagayaraj. P, Madhavan. J, Physica B, 404 (2009) 295.
[5]. S. Senthil, S. Pari, R. John Xavier, J. Madhavan, Optik, 123(2011)104
[6]. P. Praveen kumar, V. Manivannan, P. Sagayaraj, J. Madhavan, Bull. Mater. Sci.,32(2009), 431
[7]. Kurtz. S.K and Perry. T. T, (1968), J. Appl. Phys. 39, 3798–3813.
[8]. J. Madhavan, S. Aruna, K. Prabha, J. Packium Julius, Ginson P. Joseph, S. Selvakumar, P. Sagayaraj, Journal of Crystal Growth , 293,(2006) 409