

Investigations on the Growth and Characterization of an Organic NLO Single Crystal 1-Amino 3-Nitrobenzene for Photonic Applications

A. Sarbudeen^{1*}, A. Syed Mohammed Mujaher², G. Foize Ahmad², M. Gulam Mohammed²

¹Department of Physics, Aalim Muhammed Salegh Polytechnic College, Chennai - 55, India

²P.G. and Research Department of Physics, The New College, Chennai-14, India

Abstract - Good quality single crystals of 1-Amino 3-Nitrobenzene (1A3NB) was grown by slow evaporation technique using a mixed solvent of benzene + acetone (1:2) as solvent. The grown crystals were subjected to single crystal X-ray diffraction analysis in order to reveal its crystal structure and unit cell parameters. The FT-IR spectral analysis was carried out in order to confirm the presence of expected functional groups. The UV-vis analysis was done for 1A3NB single crystals to determine the optical transparency. The mechanical stability of 1A3NB single crystal were studied using Vicker's micro hardness test on prominent plane at different temperature to reveal the anisotropic nature.

I INTRODUCTION

Nonlinear optical (NLO) properties are a major probe of the electronic and solid-state structure of organic compounds and as a consequence find various applications in many areas of optoelectronics [1]. These properties lead to applications such as all-optical switching, optical power limiting, image manipulation, image processing, and data storage etc., [2]. The preparation of crystalline materials for second harmonic generation (SHG) requires establishing of a non-centrosymmetric arrangement of the crystal structure. As non-centrosymmetric space group is one of the major requirement for the existence of second harmonic generation activity. Organic NLO materials offer the potential of relatively low-power laser driven nonlinear optical system due to their optical properties, such as fast optical response time, non-resonant susceptibility and high second harmonic generation (SHG) nonlinearity compared to inorganic materials [3]. Most of these organic molecules show large nonlinear optical responses compared with inorganic counterparts, due to presence of the electron-donor and electron-acceptor groups located at the extreme of a system involving correlated and high delocalized π electron states. The preparation of perfect single crystals of preferred dimensions is found to be difficult when compared with its inorganic counterparts due to the effect of organic solvents on the growth and the habit of these highly polar materials is very significant [4]. Organic solvents often yield crystals with various habits from needles to prismatic crystals depending on the factors such as, chemical nature, solubility, polarity, evaporation rate

and other properties [5]. This effect is mainly because of the interaction of these solvent molecules on the surface of the growing crystal. Also, the chemical nature of the solvent decides the quality of the growth in most of the cases. The primary condition for the selection of suitable solvent for the growth of a particular material is its solute solubility in the crystallization temperature range [6]. The title material, 1-Amino 3-Nitrobenzene (1A3NB) also known as m-nitroaniline with molecular formula $C_6H_6N_2O_2$. In this present communication, we are reporting on the growth of 1A3NB single crystals from a mixed solvent with well settled facets and investigations on the characterization of 1-Amino 3-Nitrobenzene single crystals with a special emphasis on exploring their structural, spectral, optical, laser stability, thermal and nonlinear optical properties. We are also reporting, the temperature dependent mechanical properties and particle size dependency of the title material with a detailed discussions.

II EXPERIMENT PROCEDURE

A. Material synthesis

Single crystals of title compound was synthesized by dissolving the calculated amount of commercially available, 1-Amino 3-Nitrobenzene (1A3NB) (SRL CHEM, AR grade) in a mixed solvent of benzene + acetone (1:2) ratio. The choice of mixed solvent have modified the habit of 1A3NB single crystals to appear as an octahedron of a long rhombus. The single crystals of 1A3NB have been found to have good morphology while comparing with the previous reports [7, 8].

B. Crystal growth

The synthesized product was purified by further recrystallization process. The recrystallized salt was slowly added to the mixed solvent of benzene + acetone (1:2) ratio. The resultant solution was a pale orange colored. The solution was stirred continuously at room temperature with an immersible magnetic pedal for nearly 8 hours in order to achieve homogeneity. The solution was then filtered and kept at undisturbed. Care was taken to cover the beaker with an aluminum foil in order to prevent the evaporation of the solvent during the entire process. Good quality

single crystals of 1A3NB with perfect habit was harvested after a period of 25 days by slow evaporation technique and is shown in Fig. 1.

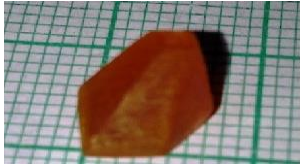


Fig. 1 Photograph of as grown 1A3NB single crystal.

C. Characterization Techniques

Single crystal X-ray diffraction data of 1A3NB was elucidated using ENRAFNONIUS CAD-4 single crystal X-ray diffractometer. FT-IR spectrum was recorded to interpret the chemical bonding and modes of vibration of 1A3NB in the range 4000–400 cm^{-1} by PERKIN–ELMER spectrometer using KBr pellet technique with a resolution of 1.0 cm^{-1} . The UV-vis transmission spectrum of 1A3NB crystal was recorded in the wavelength range 200–800 nm using Varian Carry SE model spectrometer. Microhardness analysis of 1A3NB crystals were examined by using Leitz–Weitzler hardness tester at different temperature.

III RESULTS AND DISCUSSION

A. Single crystal X-ray diffraction study

Single crystal X-ray diffraction analysis was carried using the good quality single crystal of 1A3NB in order to reveal the unit cell parameters, space group and crystal system. It is revealed from the analysis that the 1A3NB crystal belongs to orthorhombic crystal system with Pbc2_1 non-centrosymmetric space group. The unit cell parameters are found to be, $a = 6.42 (2) \text{ \AA}$, $b = 19.10 (7) \text{ \AA}$, $c = 5.03 (18) \text{ \AA}$, $V = 616 \text{ \AA}^3$ and is found to be in good agreement with the reported data [9].

B. Spectral analyses

The chemical bonding and modes of vibration of the grown compound was analyzed by recording FT-IR spectrum. The molecular structure of 1A3NB is shown in Fig. 2. The spectral analyses of 1A3NB was carried out on the characteristic vibrations of nitro group (NO_2), amino group (NH_2), benzene rings (C-C, C-H). The FT-IR spectrum of 1A3NB is presented in Fig. 3.

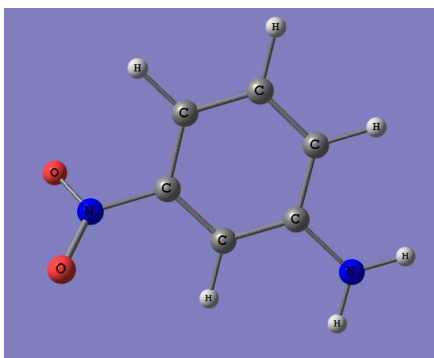


Fig. 2. Molecular structure of 1A3NB

The sharp peak found at 3429 cm^{-1} is due to N-H stretching [10]. The peak at 2931 cm^{-1} is due to very weakly bonded N-H stretching. The N-H plane bending mode is observed at 1624 cm^{-1} . The NO_2 stretching mode is confirmed by the presence of peaks at 1517 cm^{-1} , 1350 cm^{-1} and 867 cm^{-1} . The allowed vibrational frequencies arising from the C-H out of plane bending vibrations of the monosubstituted benzene ring are expected in the region $1000\text{--}650 \text{ cm}^{-1}$ [11]. The peaks at 993 cm^{-1} , 929 cm^{-1} , 867 cm^{-1} , 792 cm^{-1} corresponds to C-H bending vibrations. C-N stretch is observed at 1089 cm^{-1} . The aromatic C-H stretching band is found at 3032 cm^{-1} [12]. The vibration peak observed at 673 cm^{-1} indicates presence of benzene ring and is attributed to the modes of vibrations of benzene rings.

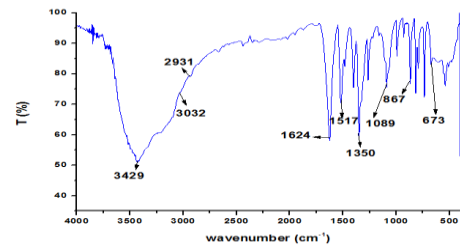


Fig. 3. FT-IR spectrum of 1A3NB

C. Optical analysis

The optical transparency and cut-off wavelength are the most important optical parameters to tailor the materials for various applications. NLO materials can be placed widely in the applications if only it has a good transparency range. As polishing of crystal plays a major role in enhancing the transparency of optical materials, the as grown crystal was subjected to polishing using alumina powder and polishing sheet. The cut and polished 1A3NB crystal of thickness 2 mm was used for UV-vis spectral study and the transmission spectrum is shown in Fig. 4. It is clear from Fig. 4, that 1A3NB single crystal has good transmittance of about 65% with cut-off wavelength 376 nm. The absence of significant absorption in the region between 376 nm and 800 nm shows that the 1A3NB crystal may be exploited for nonlinear optical applications.

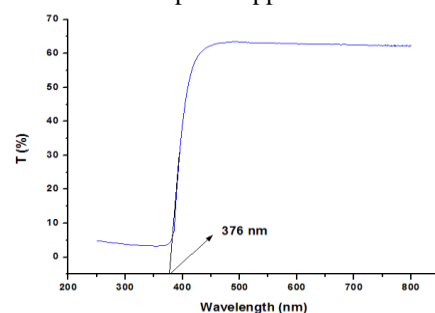


Fig. 4. Transmission spectrum of 1A3NB crystal

D. Mechanical analysis

Measurement of hardness is a useful nondestructive testing method used to determine the applicability of the crystal in the device fabrication. Microhardness study was carried out on 1A3NB single crystal using a Vickers microhardness tester fitted with a

Vickers diamond pyramidal indenter in order to evaluate its mechanical stability. The static indentations were made at room temperature and 333 K with a constant indentation time of 5 s for all indentations. A cut and polished sample of 1A3NB was used for the study. The indentation marks were made on the flat, smooth and prominent faces by varying the load from 10 to 60 g at room temperature and 333 K. Since the 1A3NB crystal melts at 115 °C the crystal was heat treated up to 60°C. The Vicker’s Microhardness number of the title crystal was calculated using the relation,

$$H_V = 1.8544 (P/d^2) \text{ (kg/mm}^2\text{)}$$

Where, ‘H_v’ is the Vickers hardness number, ‘P’ is the applied load and ‘d’ is the average diagonal length of the indentation mark.

Plots between hardness number and load for 1A3NB single crystals at room temperature and 333 K is depicted in Fig. 5. It is clear that the microhardness number increases with increasing load .It is evident from the above plot that themicrohardness number of the crystal increases with increase in loadwhich is in agreement with the reverse indentation size effect (ISE) [13,14] and also decreases with increase in temperature. The decrease in the value of hardness number with respect to increase in temperature can be attributed to the fact that, when the temperature increases, the average inter atomic distance becomes greater than that at room temperature due to lattice vibration. This leads to more and more lattice phonon interactions which causes the breaking of bond as well reduce the hardness value [15].The maximum value of hardness number observed for 1A3NB, crystal is35.2 kg/mm² at 60 g (room temperature) respectively. The load above these values develops multiple cracks on the crystal surface due to the release of internal stresses generated locally by indentation.

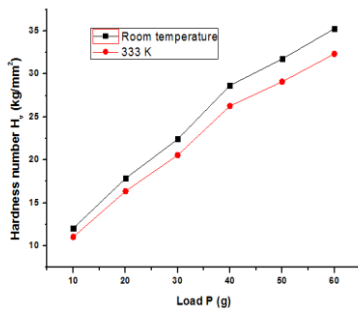


Fig. 5. Plot of hardness number vs. load for 1A3NB single crystal

The relation connecting the appliedload and diagonal length d of the indenter is given by Meyer’s law $P = ad^n$ [16], where the exponent ‘n’ called as the Meyer number, isthe measure of the Indentation Size Effect (ISE) and ‘a’, is the constant. The simplest way to describe the ISE is Meyer’s law. For the normal ISE behavior, theeponent $n < 2$.When $n > 2$, there is the reverse ISE behavior. Whenn = 2, the hardness is independent of the applied test load, and is given by Kick’s law [17].Plots obtained between log(P) and log(d) for 1A3NB single crystal at room temperature is a straight line and is shown in Fig.6. The value of ‘n’ obtained for 1A3NB single

crystal using linear fit is found to be 3.57 respectively. This is also in good agreement with RISE [14]. On careful observations made on various materials, Onitsch and Hanneman [18] pointed out that ‘n’ lies between 1 and 1.6 for hard materials, and it is more than 1.6 for soft materials. The value of ‘n’, obtained for 1A3NB single crystals is found to be 3.57, which reveals that the material is soft.

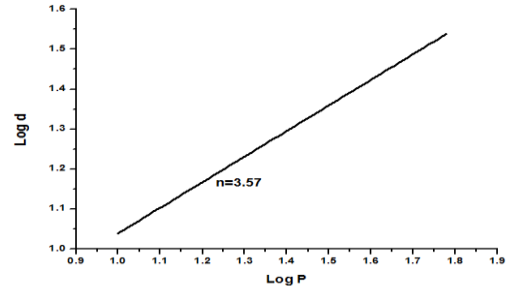


Fig 6. Plot of log P vs. log d

An elastic stiffness constant or simply an elastic constant measures how “hard” a solid is. An elastic stiffness constant (C₁₁) for the title compounds were calculated using the Wooster’s empirical formula $C_{11} = H_V^{7/4}$.

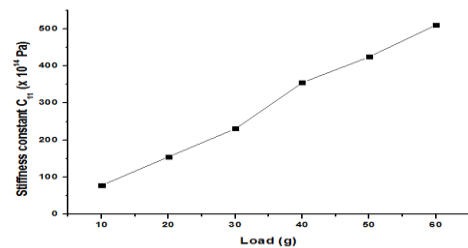


Fig.7 Stiffness constant vs. hardness number for 1A3NB

The plots of stiffness constant versus load P are shown in Fig.7. The trend of stiffness constant graph is similar to hardness number graph which gives an idea about tightness of bonding between neighboring atoms [19].

IV CONCLUSION

Optically good quality single crystal of 1A3NB was grown by slow evaporation technique. A prismatic habit of 1A3NB single crystal was grown using a mixed solvent of benzene + acetone (1:2). The cell parameters were identified using single crystal X-ray diffraction analysis. The presence of functional groups and modes of vibrations for 1A3NB was interpreted using FT-IR. From the UV-vis analysis it was confirmed that 1A3NB crystals has a wide transparency in the range 376 - 800 nm. Vicker’s microhardness studies were performed in order to evaluate the mechanical stability at room temperature and 333 K and it is concluded that the title compound is stable till 60 g load. It is also evident from the microhardness study that the hardness value decreases with increase in temperature. Indeed, the promising crystal growth, crystal habit, characterizations, employs the title material as a potential candidate for further device fabrication and other nonlinear optical applications.

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