Growth, Optical and Microhardness Studies of 2-Aminothiazole- 3, 5-Dinitrobenzoic Acid Complex

Biju Joy
Dept of Chemistry
St. Xavier's College, Thumba, Trivandrum, India

Abstract- *Single crystals of 2-Aminothiazole 3,5-Dinitrobenzoic acid has been synthesized and good quality optical crystals were grown by slow evaporation technique at room temperature. The crystallinity nature of the grown crystal was confirmed from X-ray diffraction technique. An optical transmittance study was also carried out by UV – Vis spectra. FT-IR spectra confirm the presence of functional groups in the grown crystal. The dielectric constant was seen to increase exponentially at lower frequencies. DC conductivity studies were also taken for the crystal. The microhardness studies were carried out using Vickers hardness indenter. Photoluminescence study shows that maximum emission occurs at 435nm.*

Keywords- Optical property, Microhardness, XRD, Photoluminescence.

I. INTRODUCTION

With rapid advancement of the microelectronic and the optoelectronic industry in the country, the demand for crystals has increased dramatically during the past two decades. The requirement for better and well characterized single crystals has been a driving force behind extensive research and development in crystal growth [1-2]. Organic materials have very high hyper polarizability (β), low cost, ease of fabrication, large laser damage threshold, ultra-fast response time and great possibilities for twisting the molecular structure using molecular engineering and chemical synthesis. Also they have attracted much attention because of their application in frequency shifting, optical modulation, THz wave generation, optical parametric oscillation, optical switching, optical logic and optical memory for the emerging technologies in areas such as optical interconnections, telecommunications and signal processing [3-9].

Hassan A. Mohamed et al [10] reported the structural and optical studies of 2-aminothiazole mixed with 3,5-dinitrobenzoic acid. In the present investigation we report the powder XRD, Dielectric, Microhardness and Photoluminescence studies of 2-AT 3,5-DNB crystals.

II. EXPERIMENTAL

In the present investigation the title compound was synthesized by dissolving 2-Aminothiazole and 3,5-Dinitrobenzoic acid in equimolar ratio using THF/Methanol Mixed solvents. The product was stirred well and filtered twice using whatmann filter paper to remove the impurities and covered with thick paper with perforated lid in order to control evaporation rate. Slow evaporation technique was employed to grow the single crystals. After 15 days good quality of crystals were harvested from the mother solution. The grown crystal is shown in Figure 1.

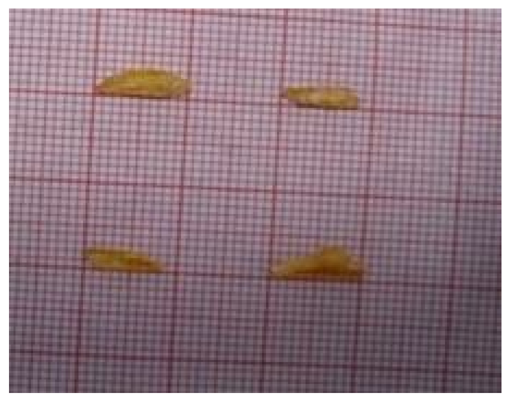

Fig. 1. 2AT- 3,5DNB single crystal.

III. RESULTS AND DISCUSSION

A Powder X-Ray Diffraction Analysis

Powder X-ray diffraction study was carried out for the grown crystal by employing SEIFERT JSO DEBYEFLEX diffractometer with Ni filtered CuKα (Wavelength λ=1.5405 Å) radiation. The powdered sample was scanned over the range 5-90° at a rate of 1°/min. The powder X-ray diffraction spectrum is displayed in Figure 2. The sharp intense peaks on the pattern reveal that the crystallites are pure and dislocation free.

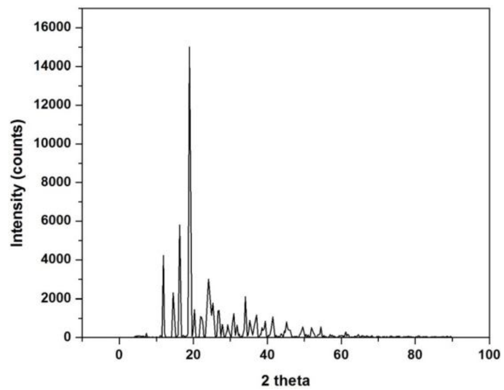

Fig. 2. Power XRD Spectrum of 2 AT - 3, 5 DNB Crystal.

B UV – Visible Transmittance Studies

The transmittance spectra of the grown crystals were recorded in the wavelength region from 200-1100 nm using PerkinElmer Lambda 35 UV-Vis spectrometer. The scanned spectrum is displayed in Figure 3 and the spectrum shows the crystal is transparent in the entire visible region. This makes the crystal a potential candidate for optical applications [11].

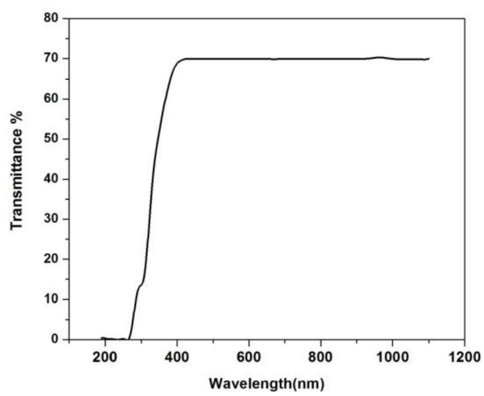

Fig. 3. UV- Vis transmission Spectrum.

C FT-IR Analysis

The FT-IR spectra of 2-AT 3,5-DNB crystal were recorded in the wave number range of 4000 to 450 cm^{-1} using the KBR pellet technique. The observed peak at 3292.19 cm^{-1} is assigned to OH stretching vibration. The peak broadening in this region is assigned to the intermolecular hydrogen bonding. The NH stretching vibration is observed at 3112 $cm^{-1.}$ C=O stretching vibrations are observed in the range of 1866.01 and 1620 cm^{-1} respectively. NO stretching vibration occurs at 1420 and 1345 cm^{-1} also it is assigned to CN stretching modes. CH out-of-plane bending vibration takes place in the region of 919.08 cm^{-1}. The FTIR absorption spectrum of 3,5-DNB is shown in Figure 4.

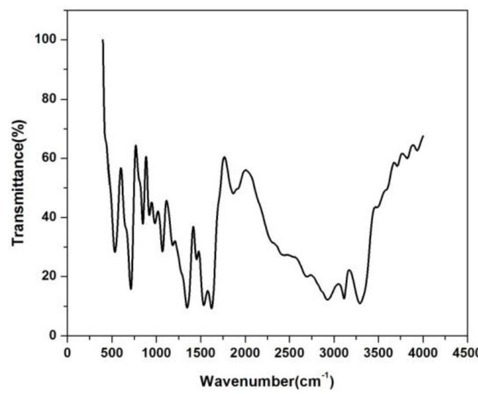

Fig. 4. FT-IR Spectrum of 2 AT - 3, 5 DNB Crystal.

D Dielectric Studies

The grown crystal is Polished and silver plated on the opposite faces were two probe connected to a 3532-50 Hioki LCR Meter (Japan). Dielectric Constant and dielectric loss were recorded at room temperature Figure 5 and 6 shows the variation of dielectric constant and loss with log frequency. The dielectric constant of the crystal was calculated using the relation [12],

$$\varepsilon_r = \frac{Cd}{\varepsilon_o A}$$

where, *C* is the capacitance, *d* is the thickness of the crystal, ε_o is the permittivity of free space (8.85x 10^{-12} Farad/m) and *A* is the area of the crystal. The dielectric constant is very high at lower frequency range and found to decrease with the increase in frequency due to the presence of space charge polarization [13, 14]. The dielectric loss is very low at high frequency this shows that the crystal contains low level defects. The low value of dielectric loss at high frequency suggests the sample posses an enhanced optical quality which is of vital importance for optoelectronic applications [15]. DC conductivity of the grown crystals was carried out using Keithley 6517B electrometer at different temperature (Fig. 7). Measurements were recorded while cooling the sample. From the figure it is observed that electrical conductivity increases with increase in temperature. This ohmic behavior confirms the semi conductor nature of the crystal.

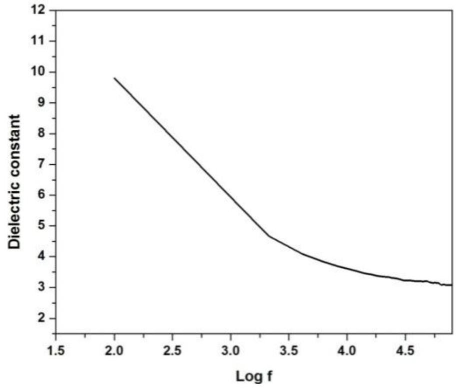

Fig. 5. Dielectric constant Vs log f.

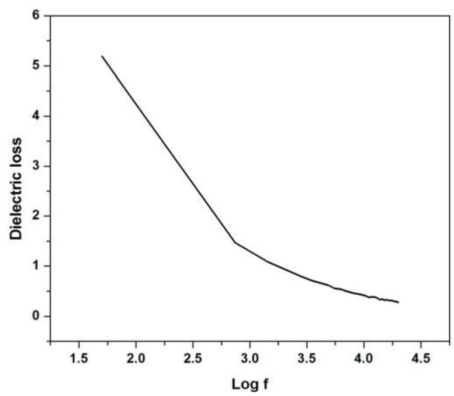

Fig. 6. Dielectric loss Vs log f.

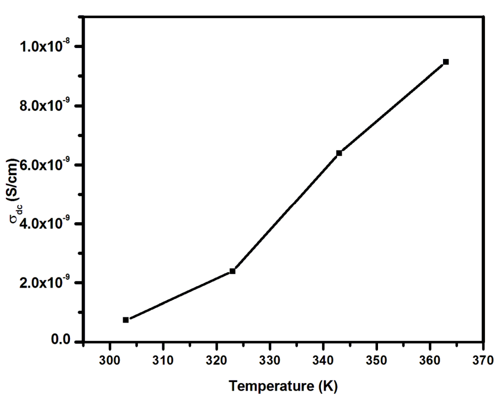

Fig. 7. DC conductivity Vs temperature.

E Microhardness Studies

Vickers microhardness test was carried out for the grown crystals. The measurements were made at room temperature at constant indentation time of 5s. Indentation impressions were measured using leitz Wetzlar miniload hardness tester, fitted with a diamond pyramidal Vickers indenter. The microhardness was calculated using the formula $H_v=1.854p/d^2$ (kg/mm^2) [9]. Where p is the applied load in kilogram and d is the diagonal length of the indent in mm for applied load above 100g micro cracks were observed around the impression [16, 17]. It is observed from the Figure 8 that when load increases hardness also increases this may be due to the release of internal stresses.

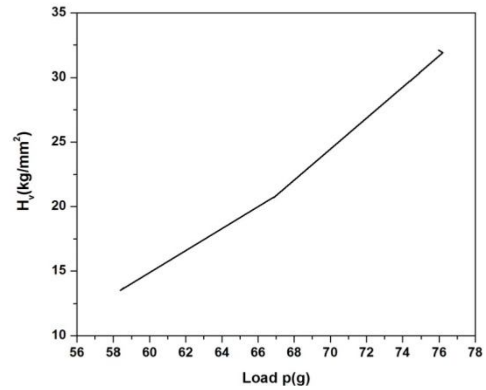

Fig. 8. Vickers hardness Plot.

F Photoluminescence

Fluorescence may be expected generally in molecules that are aromatic which contains multiple conjugated double bonds with a high degree of resonance stability. The emission spectrum was recorded in the range of 200–1200 nm at room temperature. Spectra are displayed in Figure 9 and 10. The sample was excited at 233 nm. The emission spectrum was measured in the range 250–500 nm. The maximum emission wavelength is observed to be at 435 nm. The results indicate that 2 AT 3,5 DNB crystals have a blue fluorescence emission. Also 2 AT 3,5 DNB crystals shows low UV absorption throughout the entire visible region which posses the crystal a suitable candidate for optical applications. The direct band gap of the material was calculated using the relations h, c, λ (Eg=2.852 eV).

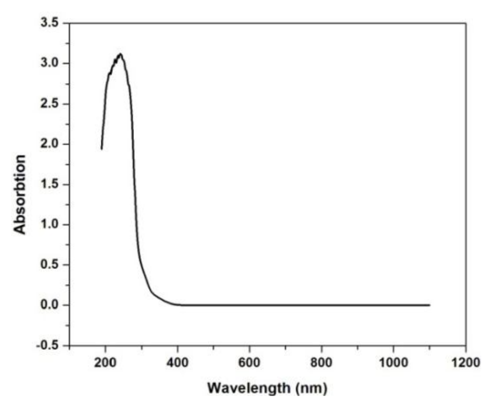

Fig. 9. Excitation spectrum of 2AT, 3,5-DNB Crystals.

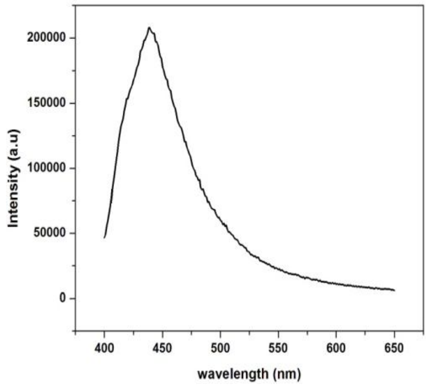

Fig. 10. Emission spectrum of 2AT, 3,5-DNB Crystals.

IV. CONCLUSIONS

The 2-Aminothiazole and 3,5-Dinitrobenzoic acid complex has been prepared and grown by slow evaporation technique. The UV–Visible spectrum reveals that the grown crystals have a cut-off wavelength of 240 nm, which can be employed in the optical applications in the entire visible region and the near IR region. The presence of various functional groups was confirmed by FT-IR spectrum. Powder X-ray diffraction studies confirm the crystallinity and show that 2-AT 3,5-DNB crystal has monoclinic structure. Dielectric constant increases in the lower frequency and the low value of dielectric loss indicates the purity of the crystal. The Microhardness value increases with the applied load. From photoluminescence study the direct band gap of the material has been calculated and crystals have a blue fluorescence emission.

REFERENCES

[1] B. K. Sarojini, B. Narayana, B. V. Ashalatha, J. Cryst. Growth, 2006, 295, 54.
[2] G. Anandha babu, K. Thirupugalmani, P. Ramasamy Cryst. Res. Technol. 2009, 44, 675.
[3] Slawomir Grabowski, Ivar Olovsson, J. Mol. Structure, 2001, 597, 6771.
[4] K. Thamizharasan, S. Xavier Jesu Raja, Francis P. Xavier, P. Sagayaraj, J. Cryst. Growth, 2000, 218, 323.
[5] S. Senthil, S. Pari, P. Sagayaraj, J. Madhavan, Physica B, 2009, 404, 1655.
[6] P. Srinivasan, T. Kanagasekaran, N. Vijayan, G. Bhagavannarayana, R. Gopalakrishnan, P. Ramasamy, Opt. Mater, 2007, 30, 553.
[7] J. Chandrasekaran, B. Babu, S. Balaprabhakaran, Optik, 2013, 124, 4296.
[8] V. Krishnakumar, M. Rajaboopathi, R. nagalakshmi, Physica B, 2012, 407, 1119.
[9] G. Anandha babu, R. Perumal Ramasamy, P. Ramasamy, Mater. Chem. Phys, 2009, 117, 326.
[10] Hassan A. Mohamed, Samir M. El-Medani, M. Ramdan, J. Indian chem. Soc, 2005, 82, 799.
[11] J. Chandrasekaran, P.Ilayabarathi, P. Maadeswaran, Optoelectron. Adv. Mater. – Rapid Commun, 2011, 5, 1325.
[12] B. Milton Boaz, R. Samuel Selvaraj, K. Senthil Kumar, S. Jerome Das, Indian J. Phys. 2009, 83, 1647.
[13] S. Brahadeeswaran, H. L. Bhat, N. S. Kim, A. M. Umarji, P. Balaya, P. S. Goyal, J. Appl. Phys. 2000, 88, 5935.
[14] J. Chandrasekaran, B. Babu, S. Balaprabhakaran, P.Ilayabarathi, P. Maadeswaran, Optoelectron. Adv. Mater. – Rapid Commun, 2012, 6, 211.
[15] R. Uthrakumar, C. Vesta, R. Robert, G. Mangalam, S. Jerome Das, Physica B, 2010, 405, 4274.
[16] E. M. Onitch, Mikroskopie, 1947, 2, 131.
[17] M. Hannenman, Metal. Manchu, 1947, 135, 23.