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Studies on the Growth and Characterization of N-methyl-4-nitroaniline Organic Single Crystal Grown by Slow Evaporation Technique

R. Lakshmi, P. Prabukanthan

Materials Chemistry Lab, Department of Chemistry, Muthurangam Government Arts College, Vellore - 632002, Tamil Nadu, India

Abstract: ***An organic material N-methyl-4-nitroaniline (NMNA) has been grown by the slow evaporation technique at ambient temperature. The grown NMNA crystal crystallized using three different solvents such as tetrahydrofuran (THF), dimethylsulfoxide (DMSO) and acetone, respectively. The grown crystal system and crystallinity were determined by single crystal and powder X-ray diffraction (XRD) analysis. Further, the grown crystals were characterized by FTIR, proton NMR, UV-Visible, micro hardness, dielectric and etching have been studied and compared. The TGA/ DTA studies indicate that the thermal behavior of the grown crystal which thermally stable up to 403 K. The relative second harmonic generation (SHG) efficiency was compared with KDP by Kurtz-Perry powder technique using Nd:YAG laser.***

Keywords: Solubility, crystal growth, powder XRD, UV-Vis-spectra and NLO property

1. Introduction

Recently the improvement of science in many areas has been achieved through the growth of organic and inorganic single crystals. Nonlinear optical (NLO) materials are expected to play a major role in the technology of Photonics including optical information processing [1-3]. So many number of research efforts showed undertaken to synthesize and characterize of NLO materials for second-order non-linear optical (NLO) applications such as high speed information processing, optical communications and optical data storage. These applications depend on the various properties of the materials, such as dielectric constant, thermal, photochemical and chemical stability. It can be useful for a variety of applications varying from modulation of optical signals. Organic materials have been of particular interest because the non-linear optical response in this broad class of materials is microscopic in origin offering an opportunity to use theoretical modeling coupled with synthetic flexibility to design and produce novel materials [4-6]. Most of these molecules show large non-linear optical responses, with the electron-donar and electron–acceptor groups located at the extreme of a system involving correlated and high delocalized π electron states [7]. There are some reports on the spectroscopic, structural and theoretical studies on the 2-methyl-4-nitroaniline [8]. The solvent effects on N-methyl-2-nitroaniline and N-methyl-4-nitroaniline [9].But there is no report available in the literature on the growth and characterization of N-methyl-4-nitroaniline. In this series, we have chosen organic compound N-methyl-4-nitroaniline (NMNA) grown by the slow evaporation technique at ambient temperature using as three different solvents such as tetrahydrofuran (THF), dimethylsulfoxide (DMSO) and acetone, respectively. In this paper, we were, reports the growth and characterized of organic single crystal of N-methyl-4-nitroaniline (NMNA) by slow evaporation techniques in different solvents at ambient temperature. The grown single crystal of NMNA was subjected to the characterization like single and powder XRD, FT-IR, proton NMR spectra, UV-Vis-, micro hardness, dielectric studies, etching studies, thermal analysis and also carried out NLO property of the sample respectively. The results of these investigations are discussed in this paper.

2. Materials and Methods

2.1 Solubility and solvent effects on growth mechanism

The significant characteristic for better yield of crystal is the solubility of the compound. Commercially available N-Methyl-4-nitroaniline (Sigma-Aldrich) of reagent grade is used for crystal growth purpose. Before starting crystal growth, solubility of N-Methyl-4-nitroaniline (NMNA) in polar and non-polar has been determined at room temperature. High solubility was polar solvent (tetrahydrofuran (THF), dimethylsulfoxide (DMSO) and acetone. Whereas for non-polar solvents (hexane and 1,2 dichlorobenzene) the solubility is considerably low. The polar solvent such as THF and DMSO their solubility's were found to be higher, but the growth rate was very slow (more than a week). But in the case of acetone solvent crystal owing to faster growth, good yield and high transparency and the solubility data's were given in Table.1.

Table 1: Effect of solvents on the growth of N-methyl-4-nitroaniline single crystals

Type of Solvents	Maximum soluble in 100ml (grams)	Crystal habit	Optical quality
Polar Solvents Ethanol	1.5	Thin needle	Transparent
Methanol	>0.5	Very thin needle	Transparent
Tetrahydrofuran (THF)	15.0	Stubbier	Transparent
Dimethylsulfoxide (DMSO)	15.8	Stubbier	Opaque
Acetone	9.5	Stubbier	Highly transparent
Acetonitile	6.0	Thin needle	Opaque
Non-Polar Solvents Hexane	>0.5	Needle like	Opaque
1,2-dichloro benzene	1.5	Very thin needle	Opaque

2.2 Crystal Growth

The crystal growth experiments were carried out by the solvent slow evaporation technique at ambient temperature. They weighed NMNA salt were thoroughly dissolved in 100 ml of tetrahydrofuran (THF) solvent containing 250ml beaker and stirred well using a magnetic stirrer to get saturated. The saturated solution was filtered using whatmann filter paper to remove suspended impurities and tightly covered by polythene paper, some holes were made in the polythene paper to achieve slow evaporation. The crystallization was allowed to take place by solvent slow evaporation at ambient temperature. The same procedure was done by another two solvent like dimethylsulfoxide (DMSO) and acetone

The obtained NMNA single crystals were transparent yellow colored with dimensions of 5 x5x0.1mm^3 has been grown for a period of 8 days using tetrahydrofuran (THF) as the solvent and in the dimensions of 5x 5x 0.1mm^{3}hasbeen grown for period of 25days using dimethylsulfoxide (DMSO) as the solvent. The crystal dimensions 13 x 9 x 0.3 mm^3 has been grown for a period of 3 days using acetone as the solvent and all the three solvent crystal photographs were shown in Figure.1(a-c).The above experimental details indicated to acetone solvent crystal has high transparency and big size of the crystal compared to other two solvent crystals.

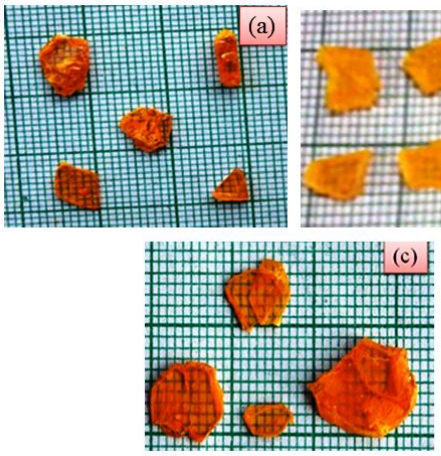

Figure 1: As-grown single crystals of NMNA at different solvents (a) THF (b) DMSO and (c) acetone

3. Characterization

The grown three crystals subjected to powder X-ray diffraction technique using GE Inspection technology model number: 3003 EP X-ray diffractometer with Cu K_α (λ=1.5406A) radiation. FT-IR spectrum of the sample was recorded in the range from 400–4000 cm $^{-1}$ for using SHIMADZU FT-IR spectrometer by KBr pellet method. The ^{1}HNMR spectrum of NMNA dissolved in deutrated chloroform and the spectrum is recorded using a 200MHz instrument. The UV-Vis spectral analysis was carried out between 500-1100 nm absorption spectrum recorded using model ELICO-SL 218 UV-Visible spectrometer. The mechanical properties of the grown crystal for various loads ranging from 10 to 100g were measured Vicker's micro hardness tester. The dielectric studies were carried out for HIOKI HITESTER model 3532-50 LCR meter and conventional two terminal sample holders in different frequency at different temperatures. The optical microscopy studies have been carried out on the etching surface of the grown crystal to investigate the defects in the crystal surface. The thermal behavior of the grown crystal was studied in TGA/DTA, 500 V20. 10 Build 36 analyzer in a nitrogen atmosphere at a heating rate of 10°C/min in the temperature ranging from 50°C to 290°C.The crystal was illuminated using a spectra physics quanta Ray GCR-2(10) Nd: YAG laser using the first harmonics output of 1064 nm with a pulse energy of up to 300 mJ. The output power of NMNA was measured and compared with the output power of potassium dihydrogen phosphate (KDP) crystal.

4. Results & Discussion

4.1Single crystal and powder X-ray diffraction analysis

The grown crystal NMNA structure was confirmed by single crystal XRD analysis. The crystal estimated to unit cell lattice parameters are a = 9.33 Å, b = 6.48 Å, c = 10.23 Å, α=90°, β=101.69° , γ=90° and V=606 A^3. From the single crystal XRD studies reveal that NMNA crystal belongs to monoclinic system.

The recorded powder XRD spectra of as-grown NMNA crystal at three different solvent employed at room temperature and the angular range 10 - 60 °C it shown Fig.2 (a-c). All the observed reflection lines were indexed by using with POWDER X software program. The appeared peaks are sharp, confirming the good crystalline nature of growing crystals. The above three solvent crystal NMNA-acetone crystal has a good crystallinity and also intensity was greater than other two solvent crystals.

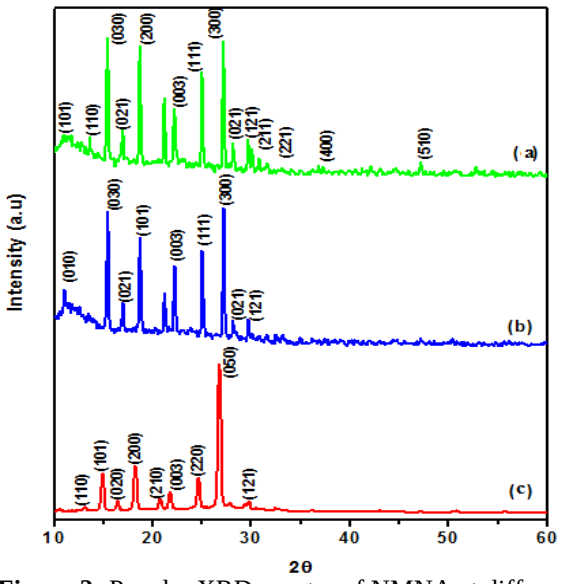

Figure 2: Powder XRD spectra of NMNA at different Solvents (a) THF (b) DMSO and (c) acetone

4.2 FTIR Spectral Analysis

Fourier transform infrared (FTIR) spectral analyses were efficiently identified the functional groups in the grown NMNA crystal. Figure 3 (a-c) shows those FTIR spectra of as-grown single crystal at three variant solvent THF, DMSO

and acetone. A broad peak at absorption in the region 3361 cm^{-1} due to NH stretching in secondary amine. The aromatic CH stretching 3012 $cm^{-1}$and broad envelope contains peaks at 2927cm^{-1} and 2837 cm^{-1} due to aliphatic methyl group stretching vibration. The absorption peaks at 1597cm^{-1} and 1458 cm^{-1} C=C stretching in aromatic ring. The NO_2 asymmetric and symmetric stretching vibration peaks appear at 1539 cm^{1} and 1288 cm^{1} respectively. The sharp peak appeared at 1099 cm^{-1} C-N stretching vibrations. The observed vibrational frequencies and their assignments are listed in Table.2. From the FTIR spectral analysis all the three solvent crystal vibrational frequencies are same and do not show any significant changes in the crystal lattice.

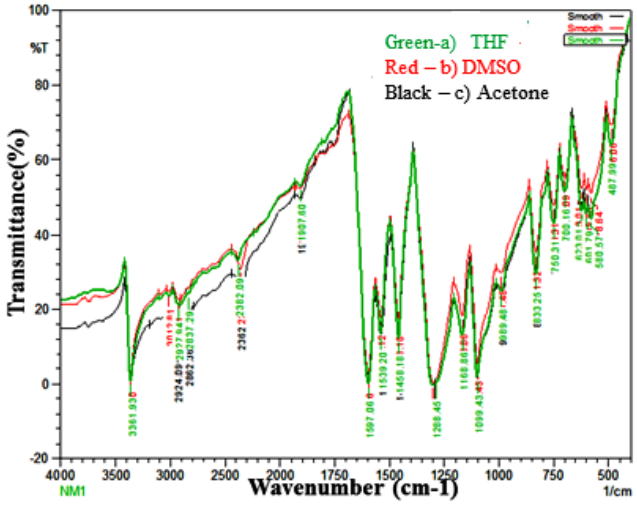

Figure 3: FT-IR spectrum of NMNA grown at different solvents (a) THF (b) DMSO and (c) acetone

Table 2: FT-IR spectral assignments of solvent variant of NMNA crystals

Wave number (cm^{-1})			*Assignments*
NMNA (THF)	*NMNA (DMSO)*	*NMNA (ACETONE)*	
3361	3360	3360	N-H stretching 2 amine
3012	3012	3012	C-Hsstretching (aromatics)
2927	2926	2922	C-H stretching
2862	2360	2862	C-H stretching(medium)
1597	1597	1602	C-C stretching in ring
1539	1541	1548	N-O asymmetric stretching
1458	1458	1463	C-H bending vibration
1288	1300	1305	N-O symmetric stretching
1168	1168	1166	C-H wagging
1099	1099	1093	C-N stretching
750	750	751	N-H wagging

4.3 Proton nuclear magnetic resonance (NMR) technique

The NMR spectral analysis is the important analytical technique used for the identified to placement of protons and molecular structure of organic compounds. The grown different solvent single crystals were dissolved in deutrated organic solvent $CDCl_3$. Figure. 4 (a-c) shows that the recorded H^1NMR spectrum of NMNA crystal. In this spectrum the appearance of four proton signals indicates the presence of four different proton environments in the NMNA crystal. The two doublets at 8.10 ppm and 6.5 ppm are assigned to the Ar-H proton. The singlet peak 4.59 ppm is assigned at NH proton. The methyl protons appear doublet at 3.09ppm. The small peak at 7.25ppm is due to the $CDCl_3$ solvent peak. From the H^1NMR spectral analysis confirmed the placement of protons and molecular structure of all the three solvent crystals are same and do not show any significant changes in the crystal lattice.

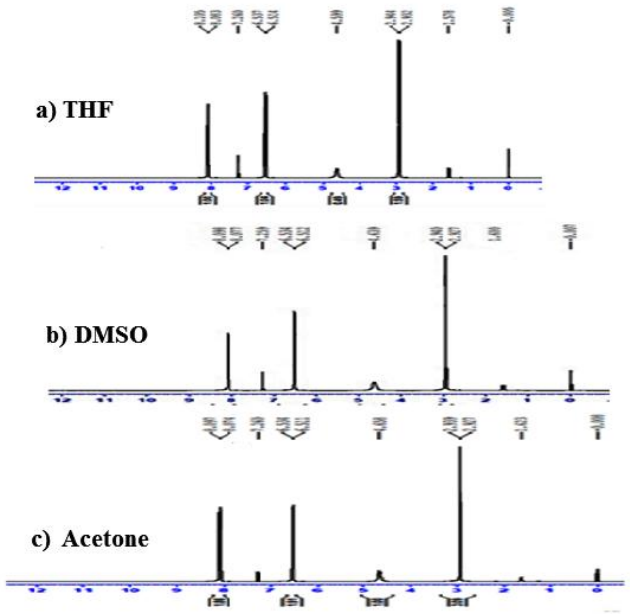

Figure 4: Proton NMR spectra of NMNA grown at different solvents (a) THF (b) DMSO and (c) acetone

4.4 UV-Vis -spectral analysis

Optical absorption data were taken on the three solvent variant crystals of NMNA samples were polished about 2 to 4 mm thickness and the wavelength range between 190 to 1100nm. The molecule absorption of UV and visible light involves transition of the electrons in the n and π orbitals from a lower energy level to higher energy level which takes place in the region of 517 - 1100 nm. Figure 5 (a-c) shows that minimum absorption of as-grown NMNA at three variant solvent THF, DMSO and acetone. From the recorded spectrum of NMNA-THF single crystal absorption edge is 517nm, NMNA-DMSO crystal absorption edge at 525nm and NMNA-acetone crystal absorption edge at 528nm. The colored compounds absorb UV-Visible light generally with a strong absorbance in the visible range [10]. The absorption band is obtained in the visible region is assigned to n-π^* electronic transition of (H_3C-NH) group present in the NMNA molecules [11].The band gap energy was calculated as-grown single crystal grown at different solvent THF, DMSO and acetone and the value were about 2.4 (THF), 2.36 (DMSO) and 2.35(acetone) eV, respectively. The above spectral details clearly indicated to NMNA-acetonecrystal was high transparency and low band gap energy compared to other two solvent crystals.

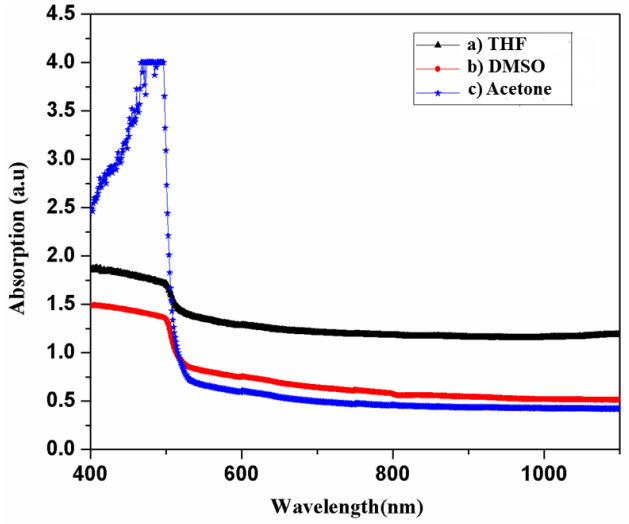

Figure 5: UV spectra of NMNA grown at different solvents (a) THF (b) DMSO and (c) acetone

4.5 Micro hardness test

The mechanical properties of the materials play an important role in device fabrication. The Vicker's hardness indentation were carried out on the grown NMNA crystals for the applied loads of 10, 25,50 and 100 g and the time of indentation is kept constant for 5 sec for trials. The Vicker's hardness value is calculated from the formula

$$Hv = 1.8544 * (P/d2)\ kg/mm^2 \quad (1)$$

Here, Hv is the Vickers hardness number in kg/mm, P is the applied load in kg and d is the mean diagonal length in mm of the indentation impression. Figure 6 (a-c) shows the variation of hardness value (Hv) with the applied load (P) of the NMNA crystal grown at different solvent (THF, DMSO and acetone). The hardness value is increases with increased load which indicates the reverse indentation size effect (RISE) [12].The value of the work hardening coefficient of all the three solvent crystal was found to be the same value as 1.72. According to Onitsch, n lies between 1 and 1.6 for hard materials, and n is greater than 1.6 for soft materials [13]. Thus, it is concluded that NMNA is a soft material category.

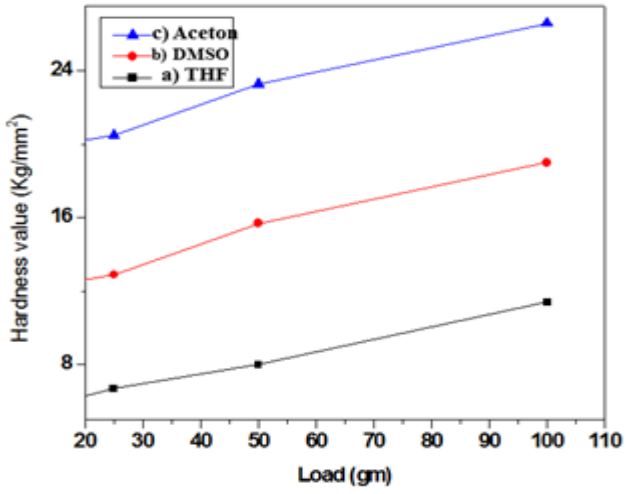

Figure 6: Variation of hardness with applied load NMNA grown at different solvents (a) THF (b) DMSO and (c) acetone

4.6 Dielectric Studies

Dielectric properties are correlated with the electro-optic property of the crystals[14]. Dielectric measurements were carried out grown at three different solvent THF, DMSO and acetone crystal using a frequency range is 50Hz to 5MHz and different temperature at 333, 353 and 373K. A sample has 3mm thickness of surfaces the crystal having silver paint it is establishing the electrical contacts. The crystal placed between the two electrodes and the measurements is carried out. The dielectric constant was calculated using the relation

$$\varepsilon = Cd/\varepsilon_o A \quad (2)$$

Here C is the capacitance, d is the thickness of the crystal, ε_o is the permittivity of free space and A is the area of the crystal. Fig. 7 (a-c) and 8 (a-c) shows the variation of the dielectric constant and dielectric loss of the as-grown single crystals at different solvent THF, DMSO and acetone with log frequency at different temperatures.

From the plot shows that dielectric constant decreases with increasing frequency and finally it becomes almost constant at higher frequencies for all temperatures and it reveals that dielectric constant increases with increase in temperatures. The measurements of dielectric loss at different temperatures and frequencies show the same method. From the plot it was observed that high values of dielectric constant at low frequencies may be due to the presence of all the four polarization namely space charge, orientation, electronic and ionic polarization. Its values at high frequencies may be due to the loss of significance of these polarizations decreases gradually [15-16]. Space charge polarization is gradually active at lower frequencies and high temperatures and indicates the perfection of the crystal [17]. It is indicated that dielectric constant increases with increasing temperature due to the space charge polarization which depends on the purity and perfection of the grown crystal [16].The low value of dielectric loss at high frequency implies that the grown NMNA single crystal possesses a lesser number of electrically active defects and this parameter is of vital importance for NLO applications [18].From the dielectric studies reveals that all the three solvent crystals dielectric properties were same and do not show any significant changes .

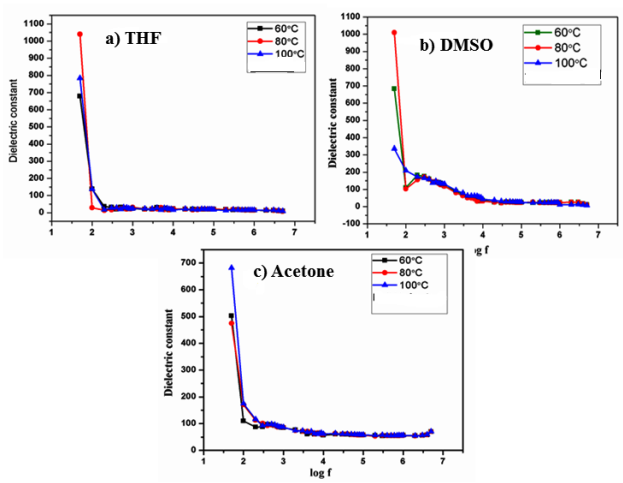

Figure 7: Variation of dielectric constant with log frequency of NMNA grown at different solvents (a) THF (b) DMSO and (c) acetone

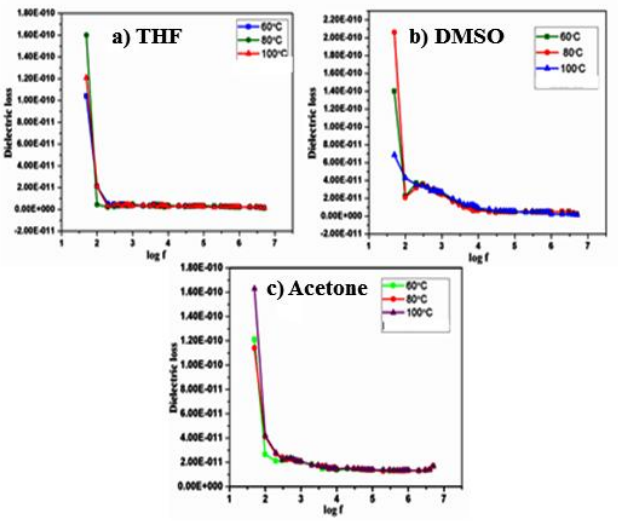

Figure 8: Variation of dielectric loss with log frequency of NMNA grown at different solvents (a) THF, (b) DMSO and (c) acetone

4.7 Etching Studies

The chemical etching study is very important characteristics to the quality of the grown crystals and also it specified the growth mechanism and crystal defects. The micro morphology studies were carried out in the grown three different solvent such as THF, DMSO and acetone crystals using pure methanol as an etchant at room temperature for the etching time of 10 sec [as-shown Figure 9 (a-c)]. The crystals were completely immersed in methanol etchant and the etched surface was dried by gently wiping them between two tissue papers and then immediately examined and their microstructures were analyzed using and optical microscope in the reflection mode. No defined pattern of growth is visible in before etching. But after etching 10 sec, the circular patterns were observed on the crystal surface. This may be due to change in the diffusion field around a dislocation site with increases of etching time. An increase in the etch time, does not change the morphology of the etch pit. On successive etching from 10 to 30 sec the circular etch patterns do not disappear suggesting that the etch pits are due to dislocations.

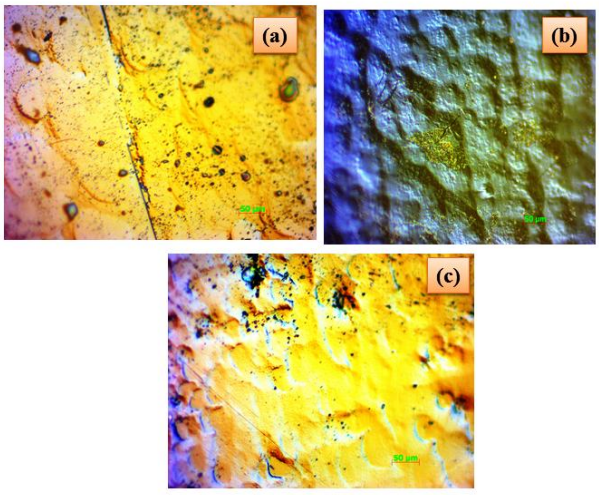

Figure 9: Etch patterns of NMNA at different solvents (a) THF, (b) DMSO and (c) acetone

4.8 Thermal analysis

Thermal property of material was carried out in thermo gravimetric analysis (TGA) and differential thermal analysis (DTA). Figure.10 shows that TGA&DTA curves for the grown NMNA samples. From the TGA curve it is observed that a single stage of major weight loss starting from 130℃ to 210°C it is due to decomposition of NMNA material. The TGA curve it is evident that the sample is stable up to 403 K.From the DTA analysis, there is no endotherm peak, but it has one exothermic peak appear at 210°C and it is due to oxidative decomposition of crystal. The exothermic peak matched with decomposition of TGA trace. The compound was melting started with 130°C and decomposition of compound completed at 230°C. From the above discussion NMNA compound thermally stable up to 403 K.

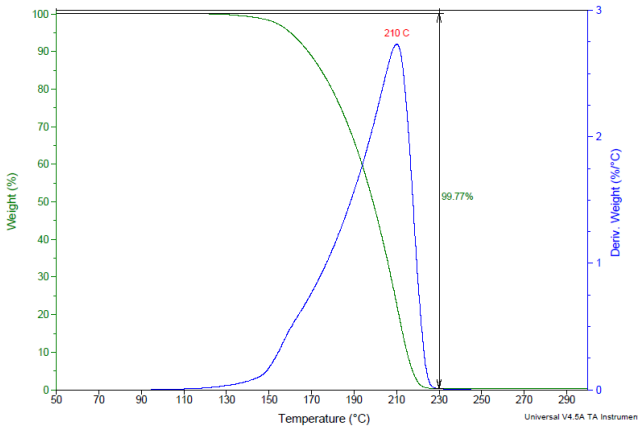

Figure 10: TGA -DTA thermo gram of NMNA crystal

4.9 Non-linear optical studies

The powdered samples are tightly packed in a micro capillary tube mounted in the path of the Q-Switched Nd: YAG laser was used as a light source. A fundamental laser beam of 1064 nm wavelength, pulse width 10 ns with 10Hz repetition rate was made to fall normally on a sample. The input energy used as300 mJ / pulse, photomultiplier tube was actively as detector and oscilloscope assembly detected the green light emitted by the sample. The second harmonic signal (λ =532) outputs are 64 mV is obtained for NMNA samples, respectively. The reference material KDP shows 55 mV of the same frequency region. The SHG conversion efficiency of NMNA crystal was divulged to be 1.16 times greater than that of reference material. An emission of green radiation exposed to NMNA crystal exhibits non-linear optical property and the crystal have a higher SHG efficiency was confirmed.

5. Conclusions

The organic single crystals of NMNA were successfully grown by slow evaporation techniques using with three different solvents like a THF, DMSO and acetone. The acetone solvent crystal has highly transparent and also big size of the crystal compared to other two solvent crystals. The single crystal X-ray diffraction study shows that NMNA crystal crystallized in the monoclinic system. The powder X-ray diffraction studies indicated to acetone solvent crystal have a high intensity and sharp peak was appeared it is conformed to it has high crystallinity compared to other two

solvent crystals. The functional groups are observed in FT-IR analysis, it is indicated there is no any significant changes in the mode of vibrations. The proton NMR spectrum shows the placement of protons and molecular structure of NMNA compound was confirmed. The UV-Vis NIR spectra show that absorption takes place in the visible region at 517, 525, 528 nm and the band gap energy was 2.4, 2.36 and 2.35 eV in NMNA-THF, NMNA-DMSO and NMNA-acetone solvent crystals, respectively. The mechanical property was evaluated by Vickers micro hardness tester all the three solvent crystal shows the n value is 1.72 so the NMNA compound is soft material. Dielectric studies revealed that the dielectric constant of the grown crystals was increasing with increasing temperature. The circular etch pits were observed in the entire three solvent crystal surface during etching. A thermal study reveals that NMNA compound thermally stable up to403 K. The NMNA crystal SHG efficiency was 1.16 times greater than that of KDP and it shows that the crystal is promising NLO material for frequency doubling and other optoelectronic applications.

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