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GROWTH AND CHARACTERIZATION OF 2-AMINO-3-NITROPYRIDINE ORGANIC SINGLE CRYSTAL GROWN BY SLOW EVAPORATION TECHNIQUE

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ABSTRACT

Organic material of 2-amino-3-nitropyridine (ANP) single crystal was grown by slow evaporation technique at ambient temperature using dimethylsulfoxide (DMSO) as a solvent. The grown crystals were subjected to various characterization studies. The powder XRD analysis shows the crystal phases and crystallinity were identified. Functional groups of the grown material were confirmed by FT-IR vibrational spectrum. The UV- Visible absorption spectrum has been recorded and it shows that cut - off wavelength at 524 nm. Dielectric measurements were carried different temperatures at 313 K to 373 K. From the dielectric studies reveals the both dielectric constant and dielectric loss were increases in lower frequency and decreases in higher frequencies. Thermal behavior of ANP compound was studied using thermo gravimetric (TG) and differential thermal analyses (DTA) it is thermally stable up to 383 K. The second harmonic generation (SHG) behavior of ANP was evaluated by Kurtz-Perry powder technique.

KEYWORDS: Dielectric studies; spectral studies; thermal study, NLO property.

1. INTRODUCTION

An organic crystal has been widely studied due to their non-linear optical (NLO) coefficients being often greater than those of inorganic materials. The organic NLO materials basic structure was based on π bonding systems. Due to the overlap of π bonding electrons, delocalization of the charge distribution takes place, which leads to a high mobility of the electron density. Organic based materials have great potential in electronics due to the ease of their design and synthesis to suit the requirements of opto-electronic technologists. In order to be useful in modern technology, the material should possess large second order optical nonlinearity, short transparency cut-off wavelength and good thermal stability. Nowadays the increasing demand on organic materials for technological applications, which includes optical frequency doublers, ultra-fast modulators, amplifiers and switches, has prompted researchers to look for newer promising materials.[1,4] This induces the researchers to discover a new class of NLO materials which should complete the needs of material science and crystal engineering fields.

Pyridine and their organic complexes exhibit a large amount of fluorescence in crystalline environment.[5] In this basis the present work, we are chosen in organic compound 2-amino-3-nitropyridine (ANP) was used to grown from dimethylsulfoxide using slow evaporation technique. The grown crystal ANP were subjected to various characterizations studies such as, powder X-ray diffraction (XRD), Fourier transform infrared (FT-IR), thermal analysis, dielectric studies and nonlinear optical property, respectively.

2. SOLUBILITY AND CRYSTAL GROWTH

Commercially available 2-amino-3-nitropyridine (ANP) (Sigma-Aldrich) of reagent grade is used for crystal growth purpose. Before starting crystal growth, solubility of ANP in polar and non-polar has been determined at room temperature. The polar solvent solubility is high such as dimethylsulfoxide (DMSO), whereas non-polar solvents solubility is significantly low. DMSO is used as solvent for growing single crystals of ANP grown by slow evaporation technique. They weighed ANP were thoroughly dissolved in 100 ml of DMSO solvent containing 250 ml beaker and stirred well using a magnetic stirrer to get saturated. The saturated solution was filtered using whatmann filter paper to eliminate suspended impurities and tightly covered by polythene paper, some holes were made in the polythene paper to achieve slow evaporation at ambient environment. Good transparent yellow colored single crystals of dimensions 14 x 1 x 1 mm^3 have been obtained in the period of 25 days and the crystal photograph shown in Fig. 1.

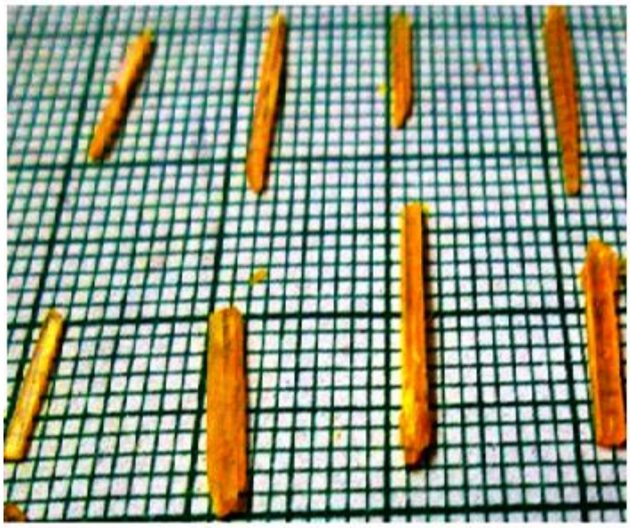


Fig. 1: Photograph of as-grown 2-amino-3-nitropyridine crystals.

3. RESULTS AND DISCUSSIONS

3.1 Powder XRD analysis

The crystalline nature of the 2-amino-3-nitropyridine (ANP) grown crystals was confirmed by powder X-ray diffraction (XRD) analysis. The grown crystal subjected to powder X-ray diffraction technique using GE Inspection technology model number: 3003 EP X-ray diffractometer with Cu Kα (λ=1.5406À) radiation. Fig. 2 shows the powder XRD spectrum of ANP compounds recorded at room temperature in a 2θ range 10˚ to 90˚. The unit cell parameters were calculated from the powder X-ray diffraction data using powder X software. Lattice parameter values and hkl values were simulated and all in diffraction peaks were indexed. The results of sharp and well-defined diffraction peaks at specific 2θ angles testimonies the crystalline nature of the as-grown single crystals.

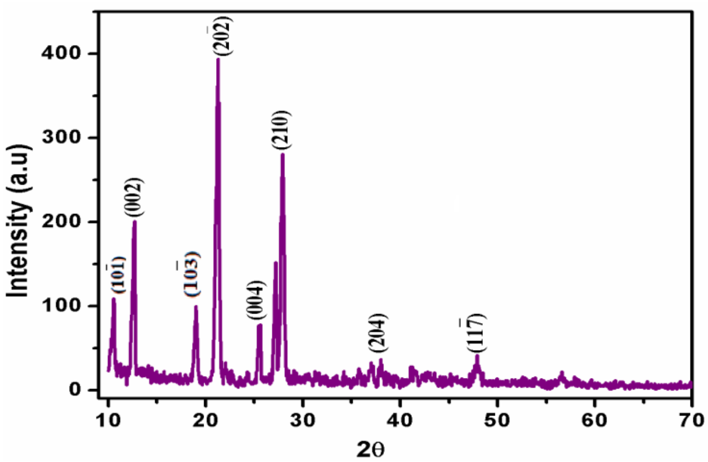


Fig. 2: Powder XRD spectrum of grown ANP crystal.

3.2 FT-IR spectral analysis

The FT-IR spectrum was recorded using with SHIMADZU spectrometer in the wave length range 400 - 4000 cm^{-1} and the sample were prepared by mixing with KBr pellet technique. KBr pellets contained a fine powder obtained from the grown single crystals. The FT-IR spectral analysis is an important tool for identifying the different functional groups. Fig. 3 shows that FT-IR spectrum of as-grown ANP single crystal. The observed band appear in frequency region of 3273 cm^{-1} assigned to N-H stretching for the primary amine group. The observed bands appeared at 1627 cm^{-1} was indicated that N-H bending vibration. The presence of asymmetric and symmetric stretching vibration of nitro group is confirmed by the peak at 1508 and 1340 cm^{-1} respectively. The aromatic ring of C=C stretching is revealed at 1435 cm^{-1}. The sharp absorption band appeared at 1070 cm^{-1} is due to C-N stretching vibrations. The observed C-H bending frequency region bands assigned at 752 cm^{-1}.

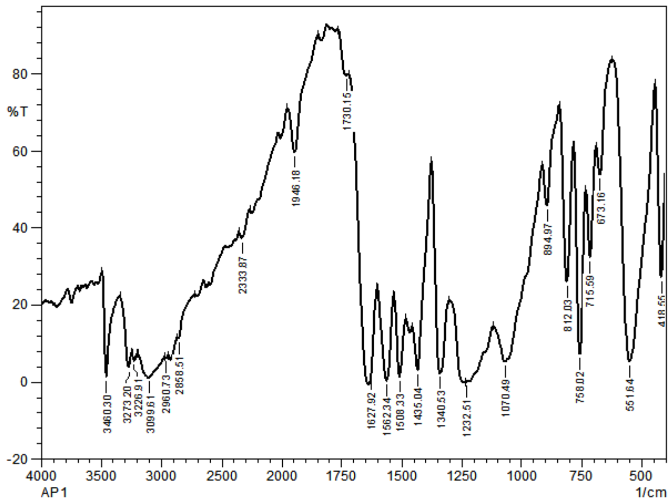


Fig. 3: FT-IR spectrum of grown ANP crystal.

3.3 UV-Vis -spectral analysis

The UV-Vis spectral analysis was carried out to grown ANP sample and the absorption spectrum recorded using model ELICO-SL 218 UV-Visible spectrometer. Optical absorption data were taken on the grown crystal was polished about 2 mm thickness and the wavelength range between 190 to 1100 nm. 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 524-1100 nm. Fig. 4 shows that minimum absorption of as-grown ANP crystal. From the recorded spectrum of crystal absorption edge is 524 nm.

The colored compounds absorb UV-Visible light generally with a strong absorbance in the visible range.[6] The absorption band is obtained in the visible region is assigned to n-π* electronic transition.[4] The band gap energy was calculated as-grown crystal 2.35 eV respectively. The above spectral details clearly indicated to ANP crystal was high transparency.

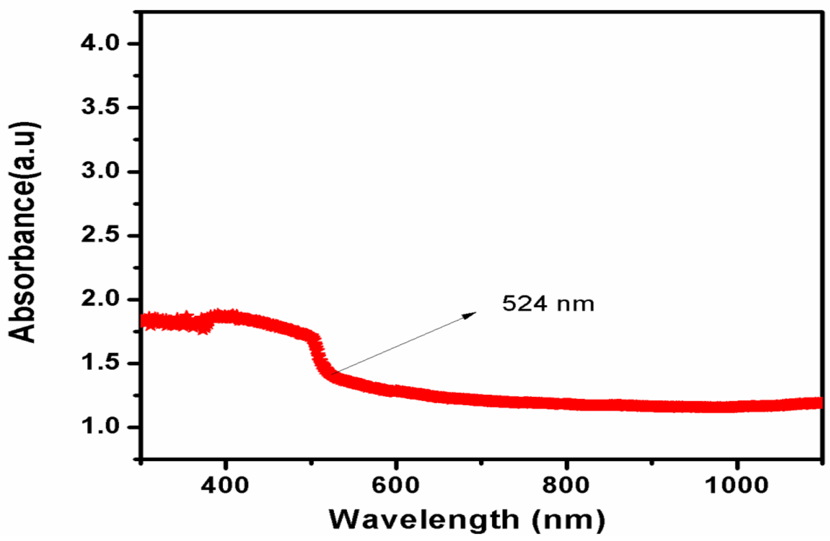


Fig. 4: UV-Vis absorption spectra of grown ANP crystal.

3.4 Dielectric studies

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 dielectric constant and dielectric loss were measured for varying frequencies under different temperature slots from 313 K to 373 K. Fig. 5 shows the variation of the dielectric constant with log frequency at different temperatures. From the plot, it was observed that the dielectric constant decreases with increasing frequency for all the temperatures. The high value of dielectric constant at low frequencies may be attributed to the contribution of four polarizations namely; space charge, orientation, electronic and ionic polarization and its low value at higher frequencies may be due to the loss of significance of these polarizations decreases gradually. At low frequency all the polarizations are active. The space charge polarization is generally active at lower frequencies and high temperatures and it indicate perfection of the grown crystal.

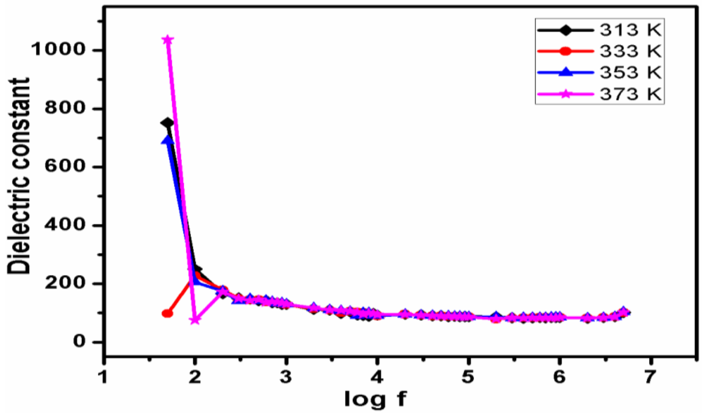


Fig. 5: Variation of dielectric constant with log frequency of grown ANP crystal.

Fig. 6 shows the variation of the dielectric loss with log frequency at different temperatures. In the figure of dielectric loss values are found to be high in low frequencies and further decreases with an increase in high frequencies. The dielectric constant and dielectric loss is inversely proportional to the frequency with all the temperatures. The behavior of low value dielectric loss with high frequency for ANP single crystals suggests that the crystal possesses enhanced optical quality with lesser defect density.

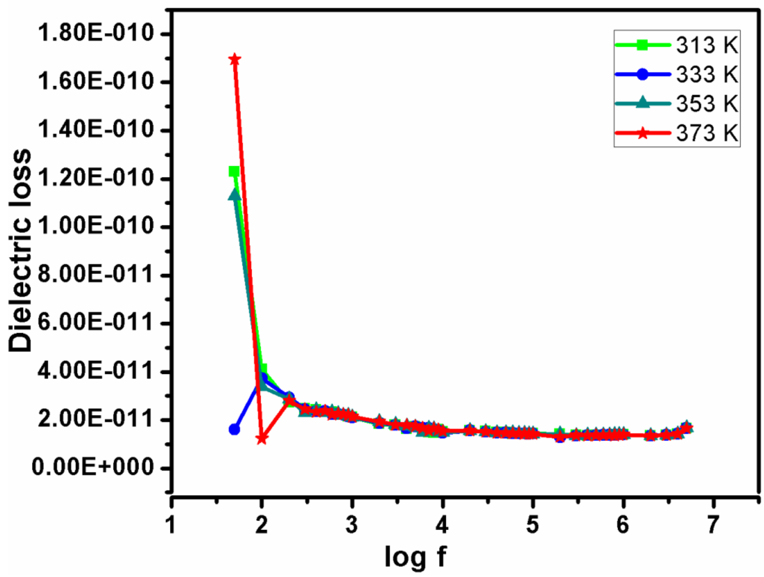
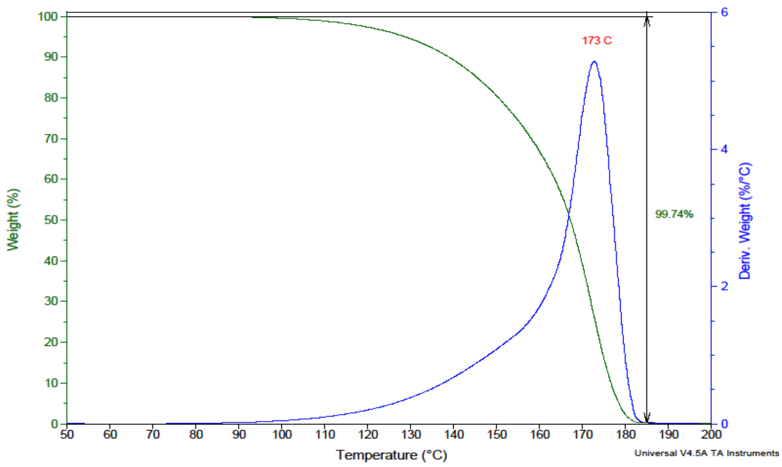


Fig. 6: Variation of dielectric loss with log frequency of grown ANP crystal.

3.5 Thermal analysis

The thermal behavior of the grown crystal was studied in TGA/DTA, 500 V20. 10 Build 36 analyzer in nitrogen atmosphere at a heating rate of 10°C / min in the temperature ranging from 50°C to 200°C. These characterizations technique used to study of the phase transition, different stages of decomposition and thermal stability of the synthesized grown crystals. Fig.7 shows that TGA/DTA curve of ANP compound.



From the TGA curve it is observed that a single stage of major weight loss starting from 383 K to 453 K it is due to decomposition of ANP material. Hence the compound decomposition temperatures were beyond 100°C and these indicate that no water of crystallization present in ANP compound respectively. The nature of weight loss designates the decomposition point of the materials.[8,10] From the DTA analysis, there is no endothermic peak, but it has one exothermic peak appear at 446 K it is due to oxidative decomposition of crystal. The exothermic peak matched with decomposition of TGA trace. The compound was melting started with 383 K and decomposition of compound completed at 453 K. From the above discussion ANP compound thermally stable up to 383 K.

3.6 Non-linear optical studies

The non-linear optical (NLO) property of the grown crystal was confirmed by Kurtz-Perry powder second harmonic generation (SHG) test. The grown crystals were characterized for their non-linear optical (NLO) property. The samples were tightly packed in a micro capillary tube mounted in the path of the Q-Switched Nd: YAG laser was used as light source. A fundamental laser beam of 1064 nm wavelength, pulse width 0.1s with 10 Hz repetition rate was made to fall normally on a sample. The input energy used as1.2 mJ / pulse, photomultiplier tube was act as detector and oscilloscope assembly detected the green light emitted by the sample. The second harmonic signal (λ = 532 nm) outputs are 25 mV is obtained for ANP samples respectively. The SHG signal generated in the crystal ANP was confirmed from the emission of bright green radiation by the crystal.

4. CONCLUSIONS

The organic nonlinear optical material 2-amino-3-nitropyridine (ANP) single crystals were grown by adopting solvent evaporation solution growth technique at ambient temperature. From the powder XRD analysis shows that crystal phases and crystallinity were confirmed. T-IR spectral studies find out the functional group of grown crystal. The UV-Vis NIR spectra show that absorption takes place in the visible region at 524 nm and the band gap energy was 2.36 eV. Dielectric studies revealed that the dielectric constant of the grown crystals was increasing with increasing temperature. The good dielectric behavior discovers a way to further advances required in the field of organic optoelectronic devices. From the TGA / DTA analysis shows that thermal stability of grown crystal found as 383 K, the thermal stability desires its use in high temperature applications. The SHG test confirms the frequency doubling of the grown crystals and its exhibit NLO efficiency.

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