SYNTHESIS, GROWTH, STRUCTURAL, OPTICAL, ELECTRICAL, PHOTOCONDUCTIVITY, Z-SCAN MEASUREMENT OF DMAP SINGLE CRYSTALS

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Abstract: Single crystals of dimethyl ammonium picrate (DMAP) were grown from a mixture of acetone and distilled water (1:1) was used as a solvent by the slow evaporation technique at constant temperature. The powder XRD confirms the crystalline nature. Third-order non-linear optical properties of the grown crystal were derived by employing a single beam Z-scan technique at a wavelength of 632 nm with He-Ne Laser system. The presence of functional groups is estimated qualitatively by FTIR analysis. The UV–Vis spectrum shows a cut-off wavelength 460nm with band gap 2.34 eV. The refractive index has been found 1.37. The photocurrent of crystals is more than that of the dark current. The dielectric loss is low at high frequency and this behavior is of vital importance for NLO applications. The full width at half maximum (FWHM) of the diffraction curves is 18 arc s, using HRXRD which is close to that expected from the plane wave theory of dynamical X-ray diffraction. Crystalline perfection is assessed laser damage threshold is observed for the grown crystal.

Keywords: Characterisation, FTIR, XRD, UV, Photoconductivity

1. INTRODUCTION:

The proton transfer between two separate NLO organic compounds takes place and results in a noncentrosymmetric organic salt, then this could increase the hyperpolarizability of both species, provided one is an acid and the second is a base. The first purposeful utilization of this strategy (proton transfer) to increase the hyper polarizabilities of the organic compounds was proposed. Picric acid derivatives are interesting candidates, as the presence of phenolic OH favors the formation of salts with various organic bases. The conjugated base, picrate, thus formed has increased molecular hyperpolariz- ability because of the proton transfer.

2. Methods and Materials:

A bulk single crystal of Dimethylammonium picrate was successfully grown by slow evaporation solution growth method [4-6]. The scope of the thesis is to concentrate the characterization of PXRD to identify the crystalline nature, UV-VIS-DRS is to find the absorbance, transmittance, reflectance and extinction coefficient hence to calculate Refractive Index, FT-IR is to identify the functional present in the crystals, Dielectric measurement is to calculate the dielectric constant, dielectric Loss and A.C Conductivity with various temperature,RXRD is to identify the crystalline perfection, Z-Scan is to identify the non-linearity of the sample, laser damage Threshold is to calculate the dislocation density and Photoconductivity is to identify the conducting nature of the sample[1-3].

In the present work, the commercially available analytical grade dimethylformamide (DMF) and picric acid (Merck, 99%) was used for synthesis of dimethylammonium picrate[1]. A mixture of acetone and distilled water (1:1) ratio was used as a solvent. The reaction scheme of DMAP is shown in Fig2.1. The prepared solution was allowed to evaporate at room temperature. After a period of 22 days well-defined,

transparent, good morphological crystals were harvested. The average size of the grown crystal is 12 mm × 5 mm × 3 mm as shown [7-9].

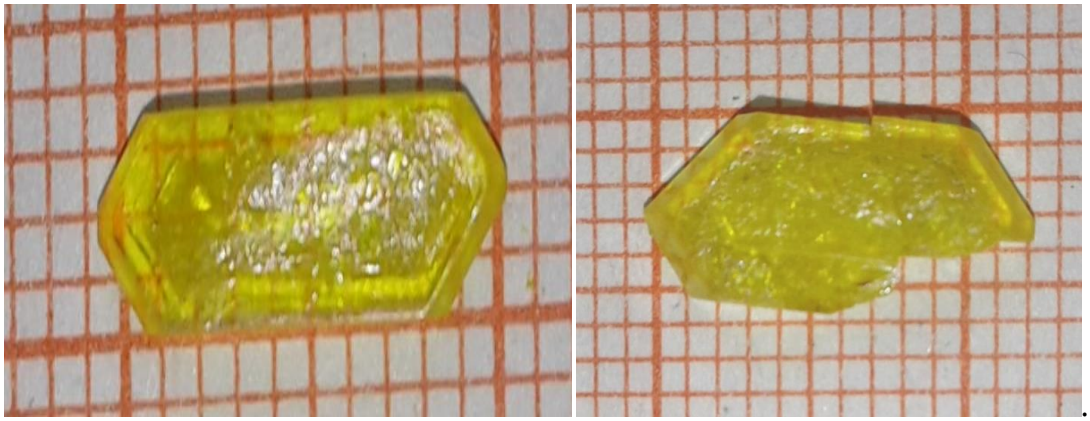


Fig: 2.1 As Grown DMAP Single Crystals

3. Results and Discussion:

The grown crystals were subjected to few characterization namely Single XRD, Powder XRD, UV-Vis Spectroscopy, FT-IR Spectroscopy and Dielectric measurement. In order to reveal the crystal structure, x-ray diffraction studies were carried out and data were collected. The unit cell parameters obtained. The crystal system is Monoclinic with P21/c Symmetry.

The grown crystals of DMAP were confirmed by single X-ray diffraction analysis using APEX.2 V2.0-2 diffractometer. The crystal belongs to the orthorhombic crystal system with the symmetry of Pca21 was reported. The lattice dimension values were indexed of the spectrum with the Index software and shown in fig 3.1. The planes (133), (233), (323), (282), (460), (184) and (2 13 1). The results were found to be in good agreement with the reported values [1].

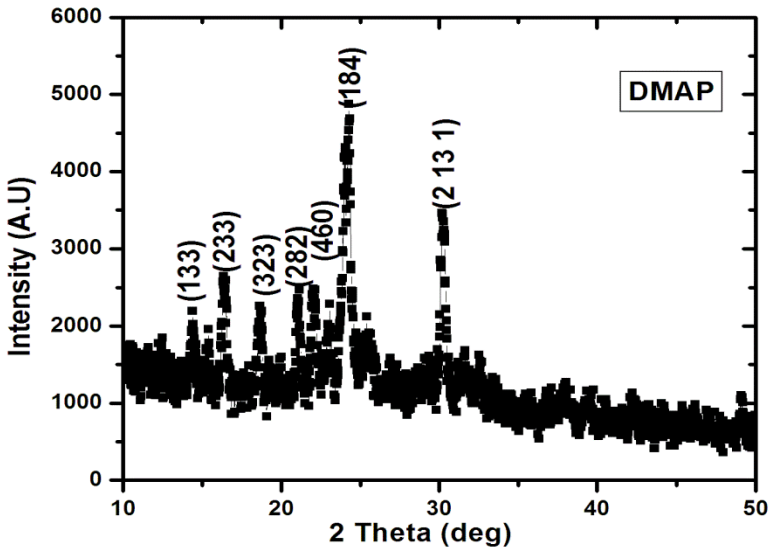


Fig: 3.1 Powder XRD pattern of DMAP crystals

Fourier transform infrared (FT-IR) spectrum was recorded using KBr pellet technique with a Perkin-Elemer RXI spectrometer. Fig. shows the recorded FT-IR spectrum of DMAP crystal in the range 400- 4000 cm^{-1} to identify the functional groups present in the grown crystal and spectrum was shown in fig 3.2.

Frequency	Assignment
3459	Phenol O-H stretching
3089	asymmetric stretching vibrations of methyl groups
2834	symmetric stretching vibrations of methyl groups
2478	Combination C–H stretching
1874	C-H aliphatic hydrocarbons
1626	NO_2 asymmetric stretching vibration
1336	NO_2 symmetric stretching vibration
1152	aromatic C–H in- plane bending vibration
1076	c-o stretching
904	NO_2 scissoring vibrational modes
711	Nitrate NO_2 bending
528	NO_2 rocking vibration

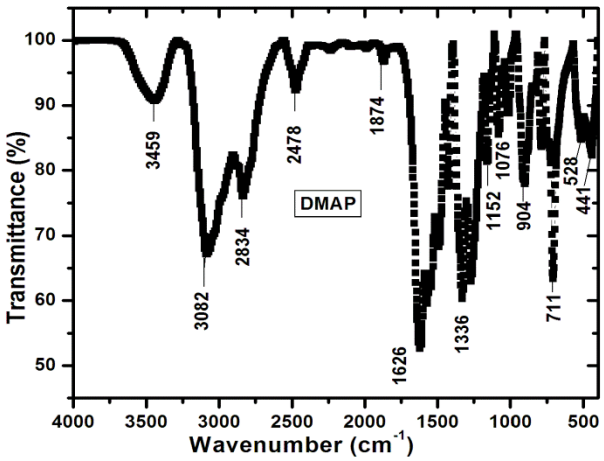


Fig:3.2 FT-IR spectrum of DMAP single crystals

Powder pellet crystals of 2mm thickenss with good optical transparent are used for analysis. UV-Vis-NIR spectrum of DMAP crystal was recorded using UV- DRS spectrophotometer varian model: 5000 in the range of 190- 2600 nm with the resolution of 0.1 nm. The recorded spectrum is shown in Fig 3.3 3.4 3.5 and 3.6. The transmission range and transparency cutoff are very important parameters, especially for crystals used in SHG. DMAP crystal presents a cutoff wavelength at 460nm. It means that DMAP crystal might be used for SHG for a 1064nm laser. The large transmittance in the all over the region makes the crystals good optical window material. The bandgap energy were calculated as 2.4eV. The results were found to be in good agreement with the reported values. [2].

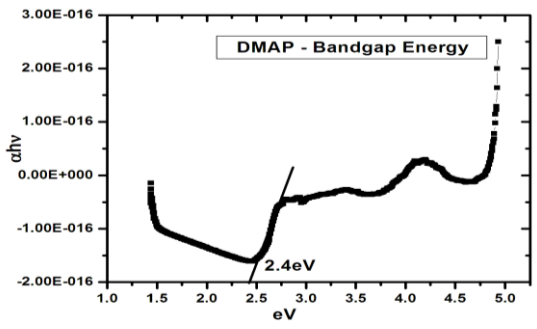


Fig 3.3 bandgap energy

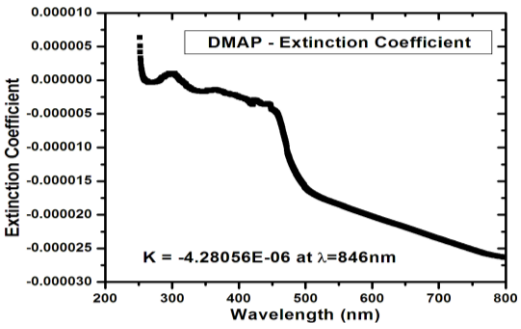
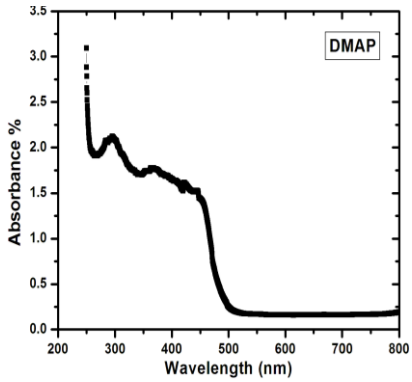
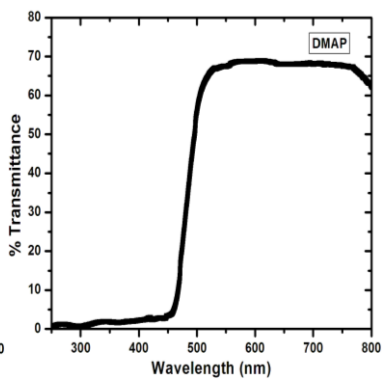


Fig 3.4 Extinction Coefficient





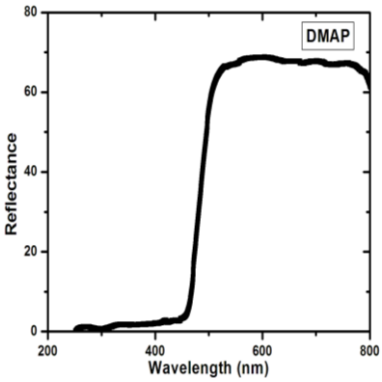
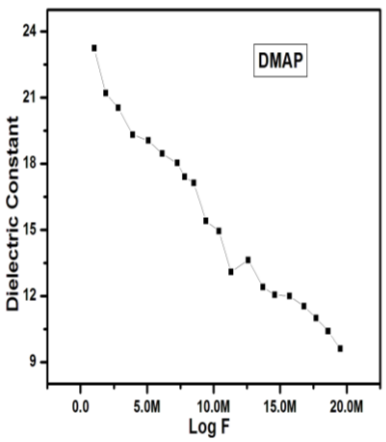
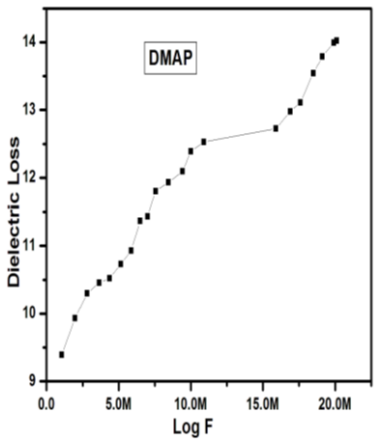


Fig 3.5 Absorption (%) Fig 3.6 Transmittance (%) Fig 3.7 Reflectance

The refractive index of DMAP crystals (cut and polished 2mm thickness with diameter 8mm) was measured by the Metricon Model 2010/M Prism coupler using the wavelength of 632nm a source of He-Ne Laser. A polished flattened single crystal is mounted on a rotating mount at an angle varied from 0 to 90 degrees. The angular reading on the rotary stage was observed, when the crystal is perfectly perpendicular to the intra-cavity beam. A laser beam strikes the base of the prism and is normally totally reflected at the prism base onto a photo detector. The crystal was rotated until the laser oscillates and the angle has been set for maximum power output. Brewster's angle of the grown crystal is measured to be 54 degrees. The refractive index of DMAP crystals has been calculated using the equation $n=\tan \theta p$, where θp is polarizing angle and it is found to be 1.376 [10].

The dielectric constant and dielectric loss were measured using Agilent 4284-A LCR meter. The dimension of 2x2x2 mm3 sample is to be used. Two opposite surfaces across the breadth of the sample were treated with good quality silver paste in order to obtain good Ohmic contact. The magnitude of dielectric constant depends on the degree of polarization charge displacement in the crystals. The dielectric Constant and loss is studied as a function of frequency for various temperatures and it is shown in the fig 3.8 3.9 and 3.10. There is variation of dielectric constant and dielectric loss dependence of high frequency region. The dielectric constant is relatively high in the lower frequency and becomes almost saturated beyond 100KHz. This may be due to the interfacial polarization. The dielectric constant, Loss and AC conductivity of the crystals were calculated. The characteristic of low dielectric loss at high frequencies clarifies that the grown samples possess enhanced optical quality with lesser defects. The results were found to be in good agreement to the reported results [2].





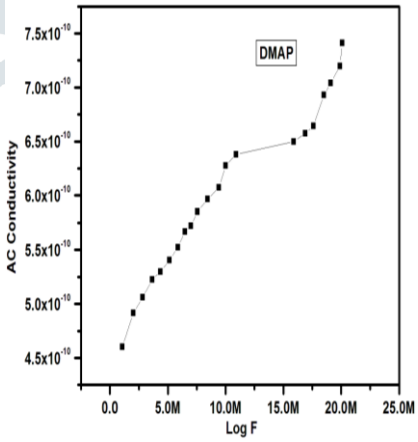


Fig 3.8 Dielectric Constant Fig 3.9 Dielectric Loss Fig 3.10 A C conductivity

Crystal perfection of the dimethyl ammonium picrate single crystal was appraised by HRXRD using a multicrystal X-ray diffractometer [2]. The well-collimated and mono-chromated MoKa1 beam obtained from the three monochromator Si-crystals set in dispersive (+,-,-,+) configuration has been used as the exploring X-ray beam. Fig 3.11 shows the high-resolution diffraction curve (DC) recorded for DMAP specimen using diffracting planes. As seen in the Fig the DC is quite sharp without any satellite peaks,

which may otherwise be observed either due to internal structural grain boundaries [11] or due to epitaxial layer, which may sometimes form crystals grown from solution [12]. The full width at half maximum (FWHM) of the diffraction curves is 14 arc s, which is close to that expected from the plane wave theory of dynamical X-ray diffraction [13]. The single sharp diffraction curve with low FWHM indicates that the crystalline perfection is very good. The specimen is a nearly perfect single crystal without having any internal structural grain boundaries. The results were found to be in good agreement in the reported values [2].

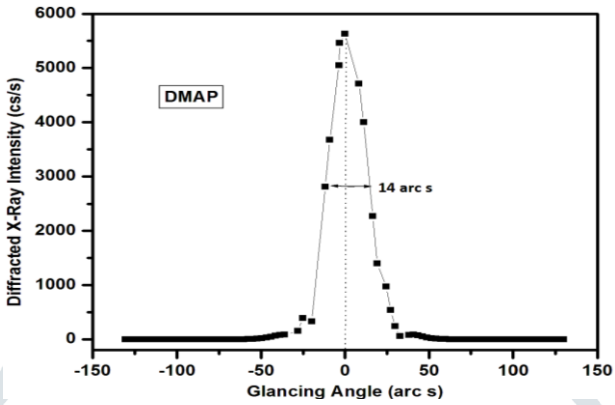


Fig:3.11. HRXRD spectrum of DMAP Single crystals.

Third-order nonlinear properties of nonlinear index of refraction and nonlinear absorption coefficient of DMAP samples were investigated using Z-scan method. Z-scan setup with laser pulses at 632 nm operating at a 1 kHz repetition rate was employed in this study. The sample thickness used in this experiment was 2 mm. The Spot size diameter in front of the aperture was 1 cm with focal length (f) was 18.5 cm/ 8.5 cm. The third-order nonlinear coefficients were estimated by measuring the transmittance of a nonlinear medium through a finite aperture in the far field as a function of the sample position Z with respect to the focal plane. The transmittance change observed as a function of the sample position Z has a peak to valley shape that is characteristic of a self focusing [11-14].

Parameter	Value
Aperture Radius	2 mm
Optical Path Distance (Z=0)	115 cm
Effective Thickness L eff	2.99 mm
linear absorption coefficient α	0.23
Nonlinear refractive index n2	4.98 x10-2cm2/W
Nonlinear absorption coefficient β	0.4 x10-4 cm/W
Linear Refractive Index n0	1.54 (no unit)
Real NLO Susceptibility $\chi(3)$	7.47 x 10-6 esu
Imaginary NLO Susceptibility $\chi(3)$	1.95 x 10-6 esu
Third-order NLO Susceptibility $\chi(3)$	8.26 x 10-6 esu

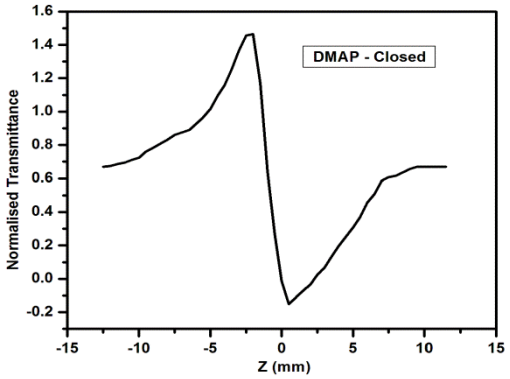


Fig: 3.12 Closed Aperture

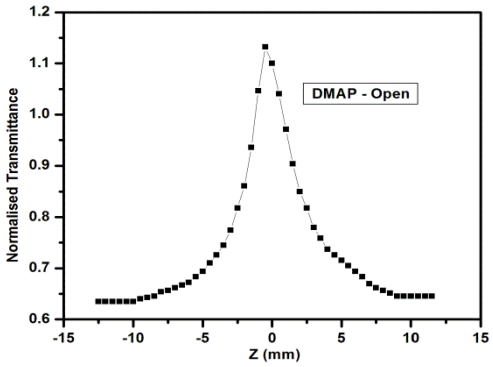


Fig: 3.13 Open Aperture

The laser damage density of DMAP crystal was measured using a Nd:YAG laser with the wavelength of 1064 nm. A fundamental wavelength, 1064 nm, with a pulse width of 10 ns and a repetition rate of 10 Hz was used. The laser beam of diameter 2 mm was focused on the crystal. The sample was placed at the focus of a plano-convex lens of focal length 30 cm. The surface damage threshold of the crystal was calculated using the expression (Pd) = E/tπr2where E is the input energy (mJ), is the pulse width (ns) and r is the radius of the spot (mm).The laser damage density of DMAP crystal was found to be 8.36 GW/cm2 for (001) plane, 9 GW/cm2 for (010) plane and 9.67 GW/cm2 for (001) plane. The results were found to be in good agreement with the reported values [2].

4. CONCLUSION:

Single crystal of Dimethylammonium picrate was synthesized from DMF and picric acid as precursors and crystals were grown by the slow evaporation technique at room temperature has been employed for the growth of non-linear optical DMAP crystal. The structural, optical, non-linear optical, laser electrical and Opto-electrical properties of the grown crystals were analyzed.

The crystalline nature, cell parameter were determined by powder XRD and it is ascertained that the crystal belongs to monoclinic system.. The presence of functional groups of DMAP has been confirmed by FT-IR analysis. The UV–visible-NIR spectrum reveals that the crystal was transparent in the entire visible region and the cut off wavelength was found to be 460 nm with band gap 2.34 eV. The refractive index has been calculated the polarizing angle of 54 deg and it is found to be 1.37. The Z-scan measurement with 632.8 nm laser pulses revealed that non-linear refractive index of the crystal is in the range of 4.98 $x10^{-2}cm^2/W$. The laser damage threshold is directly related to the impurities present in the crystal and the measured higher laser damage threshold indicates the suitability of the crystal for device fabrication. Dielectric constant, dielectric loss and AC conductivity were studied as a function of frequency at room temperature by the analysis of dielectric study. The full width at half maximum (FWHM) of the diffraction curves is 18 arc s, using HRXRD which is close to that expected from the plane wave theory of dynamical X-ray diffraction

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