Growth, Crystal Structure, Optical and DFT studies of 2-{3-[2-(4-dimethylaminophenyl)vinyl]-5,5-dimethylcyclohex-2-enylidene}-malonitrile (DAT2) crystal.

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Abstract

2-{3-[2-(4-dimethylaminophenyl)vinyl]-5,5-dimethylcyclohex-2-enylidene}-malonitrile (DAT2) is a potential candidate for generating Terahertz radiation in the range 0.1-3 THz. In the present work, we synthesized DAT2 compound and confirmed it's molecular structure by proton NMR. Good quality single crystals of DAT2 of size 1.2?0.5? 0.2 cm3 are grown for the first time, using solvent evaporation technique. The grown crystals are tested for crystalline perfection using powder XRD study and the crystal structure is determined to be monoclinic with centrosymmetric space group P21/C. The electronic band structure was studied by Density Functional Theory and the theoretical band gap was compared with experimental bandgap 1.6 eV. Further,using DFT the dielectric constants εr(ω) andεi(ω), reflectivity R(ω), refractive index n(ω), extinction coefficient K(ω), optical conductivity σ(ω) and energy loss function L(ω) for DAT2 crystal has been calculated. The results are discussed in detail

ABSTRACT

2-{3-[2-(4-dimethylaminophenyl)vinyl]-5,5-dimethylcyclohex-2-enylidene}-malonitrile (DAT2) is a potential candidate for generating Terahertz radiation in the range 0.1-3 THz. In the present work, we synthesized DAT2 compound and confirmed it's molecular structure by proton NMR. Good quality single crystals of DAT2 of size 1.2×0.5× 0.2 cm^3 are grown for the first time, using solvent evaporation technique. The grown crystals are tested for crystalline perfection using powder XRD study and the crystal structure is determined to be monoclinic with centrosymmetric space group P 2/C. The electronic band structure was studied by Density Functional Theory and the theoretical band gap was compared with experimental bandgap 1.6 eV. Further,using DFT the dielectric constants [ϵ_ρ (ω) andϵ_ι (ω)], reflectivity$R$ (ω), refractive index n (ω), extinction coefficient K (ω), optical conductivity σ (ω) and energy loss function L (ω) for DAT2 crystal has been calculated. The results are discussed in detail

Index terms: nonlinear optical material. organic compound. crystal growth DFT study. dielectric constant. refractive index

INTRODUCTION

Organic nonlinear compounds are found to be very attractive for ultrafast photonic applications such as optical switching, second harmonic generation and terahertz (THz) wave generation oweing to their high nonlinearities and ultrafast response times[1]. Organic NLO crystals like DAST,DSTMS, BNA and OH1 etc., possessing very high second order nonlinear coefficients, are presently extensively studied for generation of Terahertz between 0.1-10 THz . 2-{3-[2-(4-dimethylaminophenyl)vinyl]-5,5-dimethylcyclohex-2-enylidene}-malonitrile (DAT2) is an organic nonlinear optical material studied for terahertz generation (THz) in the region 0.1 – 3 THz[1,2]. Many explosives like RDX, TNT etc., have their finger prints in this region and hence DAT2 can be used as a suitable candidate for detection of hidden explosives [3]. DAT2 has a molecular formula of $C_{21}H_{23}N_3$. It has very high electro-optic coefficient of $r_{12} = 56$ pm/V^2.The reason of high NLO response in DAT2 arises from the electron donor in dialkylamino group and the electron acceptor is a dicyanomethylidene, >C—-C(CN)$_2$ group connected by a π-conjugated hexatriene bridge. Compared with other organic crystals, DAT2 posesses high thermal stability and good SHG efficiency. Crystal growth DAT2 by melt and vapour growth methods produced only few millimeter sized crystals, which makes it unsuitable for fabrication of optical devices. Hence, the authors are motivated in the developing large size DAT2 single crystals suitable for Terahertz applications.

The computational chemistry is an easy way to study the molecular level properties of complicated structures, their bonding interactions, electronic and optical properties etc.,(Shoba et al. 2014,)[5]. It is important to know the physical properties such as material's bandgap, dielectric constant, refractive index, conductivity,reflectivity etc.,to evaluate the performance related to optolectronic applications[6,7], Also, no quantum chemical calculations were reported for DAT2 molecule so far. Hence, the authors are interested to study the important properties such as electronic band structure, dielectric constant and linear optical properties of DAT2 crystal. In the present work, the structural, electronic and optical properties of DAT2 crystal are determined by the ab initio pseudopotential density functional method. The results are presented and discussed in detail.

II Material Synthesis and Crystal Growth : The raw materials 4-dimethyl aminobenzaldehyde, (3,5,5-trimethylcyclohex-2-enylidene) malononitrile, acetonitrile and other chemicals were purchased from Sigma-Aldrich (99.99% purity) and used for synthesis. DAT2 was synthesized by procedure[8] described in Fig. 1. 4-dimethyl aminobenzaldehyde (0.1 mol) and (3,5,5-trimethylcyclohex -2- enylidene) malononitrile (0.1 mol) were dissolved in acetonitrile (100 ml) in a round-bottomed flask. To this mixture piperidine (0.01 mol) was added and the solution was stirred at 40 C for 24 h. The product formed was confirmed by TLC plate. The resulting solution was roto-evaporated and dried. The product was purified by column chromatography using n-hexane and ethyl acetate mixture (99.99/1). The yield obtained was 37%. DAT2 was dissolved in deutrated chloroform ($CDCl_3$) and the proton NMR spectrum was recorded using Bruker instrument operating at 500MHz. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, J = 8.9 Hz, 2H), 7.01 (d, J = 16 Hz, 1H), 6.76 (d, J = 16 Hz, 1H), 6.73 (s, 1H), 6.64 (d, J = 8.9 Hz, 2H), 3.12 (s, 6H), 2.74 (s, 2H), 2.65 (s, 2H), 1.06 (s, 6H).^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.2, 155.3, 151.2, 138.3, 129.5,129.4, 124.4, 121.4,114.1, 113.4, 112.3, 75.7, 42.9, 40.3, 39.2, 31.8, 28.1.

For growing crystals of DAT2, the as synthesized salt was recrystallized twice from methanol to increase it's purity. In the present work, we attempted to grow DAT2 single crystals using methanol. But, it yielded only small sized needle type crystals. Next, the solubility of DAT2 in acetone was determined. At room temperature the solubility was experimentally determined to be 5.2 g/100ml. Saturated DAT2 solution was prepared at 40 C and allowed to cool down to room temperature by slow evaporation of the solvent. Dark-red coloured plate like DAT2 crystal of dimension 1.2 ×0.5 × 0.2 cm^3 was obtained after two weeks as shown in Fig. 2a

III Crystal structure : To identify the crystal structure and to calculate the lattice parameters of our as grown DAT2 crystals, powder X-ray diffraction analysis was carried out using Rigaku Ultimata III X-ray diffractometer. Cu Kα radiation of wavelength, 1.5405 Å was used as source for diffraction. The glancing angles were varied from 5 to 80* at the scan rate of 2deg per minute. Fig. 2b shows the Bragg's diffraction peaks obtained for powdered DAT2 sample. The experimental peaks were compared with Crystallographic

Open Database (COD no: 96-710-1371). Using hkl values, the lattice parameters were calculated a = 6.1305A, b = 7.424 A, c = 20.258 A,a = 90 , β = 96 γ = 90. he crystal structure DAT2 belongs to monoclinic with space group P 2/c.

IV Optical Reflectance:

The practical usuability of the nonlinear optical is mainly decided by the material's transparency range in the UV-Vis-IR region. Fig. 3a shows the UV–Vis reflectance spectrum obtained for the DAT2 compound in 200–1600 nm spectral region. DAT2 shows maximum reflectance of 80% between 750 and 1100 nm. The lower cut-off wavelength of the crystal was found to be 500 nm.The optical band gap (E_g) was evaluated from the reflectance spectrum as shown in Fig 3b. The optical absorption coefficient (α) near the absorption edge was estimated by using the relation,

$(a\eta\nu) = A\ (\ E_\gamma - \eta\nu)^{1/2}$————(1)

where A is a constant, E_g is the optical band gap. Fig. 3 b shows the Kubelka's plot for the absorption coefficient and the incident photon energy $(a\eta\nu\ )^2$ with the photon energy ($\eta\nu$). It can be considered as evidence for the indirect transition. The band gap value has been obtained by extrapolating the linear portion of the plot to intercept the photon energy axis and found to be 1.69 eV.

V Density Functional Theory(DFT) study

It is essential to understand the electronic structure, dielectric and optical properties of DAT2 for optoelectronic applications and hence theoretically, we performed Density Functional Theory(DFT). Wien2k software (version 18.2). was used for the present work. It utilizes a hybrid, full potential, linearized augmented plane wave (LAPW) and augmented plane wave + local orbitals (APW + lo) schemes for solving the Kohn-Sham (KS) equations of the total energy of crystalline solids[9]. The crystal structure details were obtained from CCDC Database (CCDC-27087). The muffin-tin spheres of radii 1.05, 1.10, 0.61 were assigned by Wien2k program for C, N and H atoms respectively. The nearest neighbor bond length factor of 2, local density approximation (LDA) with -5.0 Ry cut-off energy, 100 k -points,$RK_{\max}$ of 3.0 were used in the calculations. The self-consistent field (SCF) calculations were performed using the iterative procedure with energy convergence criterion of 0.1 mRy/unit cell. After SCF calculations converged, the electronic band structure, density of states, dielectric and optical properties were computed for DAT2.

Fig. 4 shows the calculated electronic band structure of DAT2. It is clear from the Fermi level shown by dotted lines (at 0.0 eV) that the maximum of valence band lies at the symmetry points in the k-space, Gamma, Z and Y. Whereas, the bottom of the conduction band lies at X and C. The corresponding energy gap is 1.5 eV. Thus, (DAT2) has an indirect band gap of about 1.5 eV. This is comparable with the experimental band gap value obtained from DRS analysis (˜1.69 eV). It is to be noted here that, in general, the underestimation of band gap energy by DFT calculations is a known fact. The calculated total density of states (DOS) of DAT2 is shown in Fig. 5 which is consistent with the electronic band structure.

Kramer-Kroning relation : The real part (ε_r) and the imaginary part (ε_i) of the dielectric constant (ε) are related as

$\varepsilon\ =\ \varepsilon_r + \ j\varepsilon_i$————————- (2)

Where, $\varepsilon_r = n^2 - k^2and\varepsilon_i$ = 2nk. Here n and k are refractive index and extinction coefficient respectively. Dielectric contributions arises either because of intra or inter-band transitions. The indirect inter-band transitions arise from scattering of phonons and their contribution is negligible to the dielectric function when compared to direct inter-band transitions.

Fig. 6 depicts the real and imaginary parts of dielectric permittivityϵ_ρ and $\epsilon_\imath$ of monoclinic DAT2 for crystallographic X and Y-axes. The first excitation peak at 1.6 eV is due to the excitation of an electron from the occupied valence band to the unoccupied conduction band. From the graph, it is clear that both real and imaginary part of dielectric constant increase with the increase of photon energy upto bandgap value of 1.69 eV. The imaginary part of the dielectric permittivity increases linearly with a higher value than

the real part. The dielectric loss is maximum at 1.5eV. The static dielectric constant is 23 for XX direction and 18 for YY direction. The DAT2 shows dielectric behaviour until 1.7 eV and thereafter it behaves as metallic nature. The low value of dielectric constant proves DAT2 as a suitable candidate for ultrafast photonics applications. Further, from the imaginary part of dielectric constant, reflectivity R (ω), optical conductivityσ (ω), refractive index n (ω), extinction co-efficient$k$ (ω), absorption co-efficient$I$ (ω) and energy loss function$L$ (ω) [9] were calculated.

Reflectivity $P(\omega)$: When electromagnetic radiation is incident on a material medium, it oscillates the electron clouds, and if there is no scattering, the radiation gets reflected totally. Above plasma frequency, reflection declines and transmission start to dominate. Fig. 7a represents the reflectivity spectraR_{xx} (ω) andR_{yy} (ω) as a function of energy E . The static values of reflectivity are 65 % for XX and 55% for YY direction at 1.7 eV. Three peaks were seen at 4.5, 6.7 and 9.5 eV. These peaks occur due to inter molecular excitations. For higher energy (14 eV) both XX and YY direction show 50% reflectivity for DAT2.

Optical conductivity $\sigma(\omega)$: The electronic states of materials can be studied using optical conductivity. A perfect dielectric is a material that has no optical conductivity. According to the multi-component model, the real part of the optical conductivity (σ) of the crystal can be calculated using the following relations

$$\sigma(\omega) = \frac{\omega}{4\pi} \operatorname{Im}(\varepsilon) \text{———— (3)}$$

The optical conductivity is calculated to be 1.5 eV, and it increases rapidly due to the high density of electrons. Several peaks are observed which corresponds to bulk plasmon excitation. The main peak was located at 1.7 eV, where the optical conductivity value is about the order of 10^{15}(Siemens/m) The variation in the real and imaginary part of optical conductivity is depicted in Fig. 7b. The conductivity decreases as the photon energy E increases. The real part of conductivity shows maximum peaks at 2.5, 5eV and 7 eV.[10]

Refractive index $n(\omega)$: The refractive index valuesare required for estimation of

phase matching condition for efficient Terahertz generation. Fig. 8a shows the refractive index as a function of photon energy (E). The static refractive index (zero photon energy) has two values as principal axes namely 2.1 for (XX) and 2.3 for (YY) direction. The$\nu(\omega)$ tends to increase linearly and attains maximum in the visible region (1.5 eV) and decreases in UV region. Refractive index attains a minimum around 5 eV. The extinction coefficient$\kappa(\omega)$ shows peaks at 1.6 eV. The refractive index values in each crystallographic direction indicate that DAT2 is an optically anisotropic and suitable for phase-matched THz applications.

Electron Energy Loss, $L(w)$: Fig 8b describes the energy loss of a fast electron traversing in DAT2. The peaks in the EEL(ω) spectra represent the characteristics associated with the plasma resonance, and the corresponding frequency is the so-called plasma frequency, above which the material is a dielectric ($\varepsilon_1(\omega)>0$) and below which the material behaves like a metallic compound ($\varepsilon_1(\omega)<0$). The energy loss is minimum at 4 eV. The electron energy loss spectrum shows five distinct peaks at 2.2, 3.2, 5.8, 8 and 9.8 eV. The maximum energy loss leads to a decrease in reflectivity.

VI CONCLUSION

DAT2 compound was synthesized using one step Kneogevel condensation method using 4 dimethyl amino benzaldehyde and (3,5,5-trimethylcyclohex-2-enylidene) malononitrile. Large size, optical quality DAT2 single crystals were grown from acetone using solvent evaporation process. From powder X-ray diffraction pattern, the crystal structure of DAT2 was found to be monoclinic with space group $P2_1$. The lattice parameters are a = 6.1305 Å, b = 7.424 Å, c = 20.258 Å, $\alpha = 90$, $\beta = 96$ $\gamma = 90^\circ$. The transparency range of DAT2 extends from 800-1100 nm. From the reflectance spectrum, the optical band gap was calculated to 1.69 eV whereas optical bandgap of 1.5 eV was obtained from DFT calculation. We studied the electronic structure and electronic charge density for DAT2. Our calculated electronic charge density repots strong sharing of electrons between C/N with H atoms. The dielectric constant value was found to be 15. Maximum reflectivity of 65% was found at 1.7eV. The static values of refractive index are 2.1 and 2.3 for XX and YY plane respectively. The magnitude of conductivity is found to be of the order of 10^{15}. The energy loss

is minimum at 4 eV. The calculated results of the optical properties shows that the DAT2 is suitable for optoelectronics and ultrafast photonics applications.

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Figure captions:

Fig. 1 Synthesis route of DAT2 using Knogvel condensation method.

Fig. 2(a) Image of as grown single crystal of DAT2 from solvent evaporation

Fig. 2 (b) Powder X-ray diffraction forpattern for DAT2

Fig 3(a) Optical absorbance spectrum of DAT2

3(b) Kulbeka-Munk plot for estimation of optical bandgap (Eg)

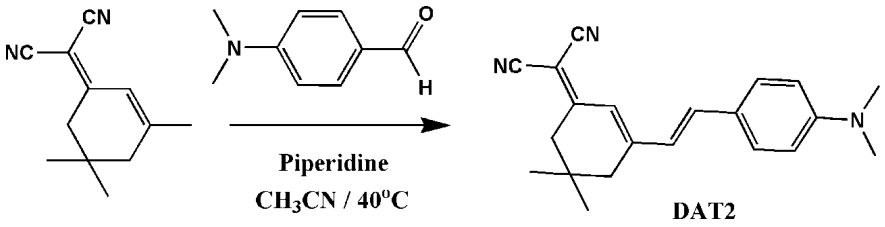
Fig. 4 Calculated electronic band structure of DAT2

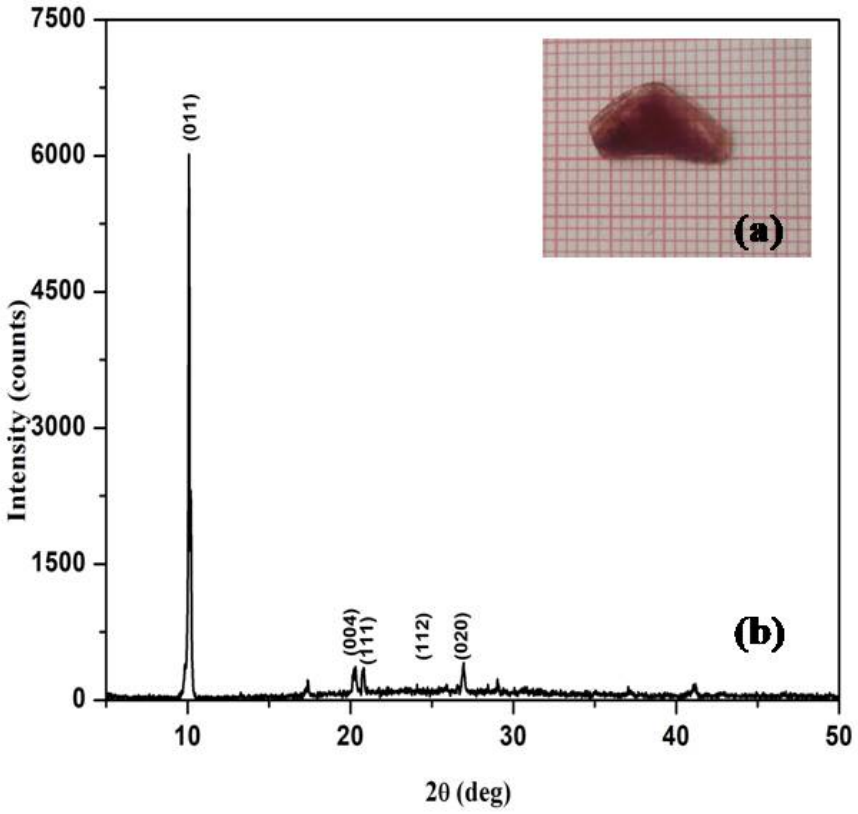
Fig. 5 Calculated total density of states of DAT2

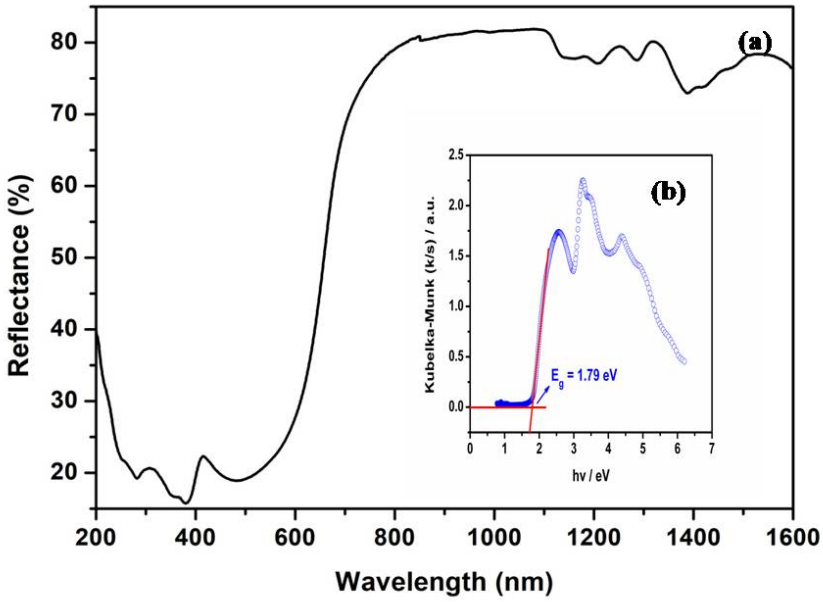
Fig. 6 Kramer Kroning relation for DAT2

Fig. 7 Calculated (a) reflectivity, R(ω) (b) optical conductivity, σ(ω)

Fig. 8 (a) refractive index, n(ω) (b) energy loss, L(ω) of DAT2







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