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Optical and dielectric studies on organic nonlinear optical 2-furoic acid single crystals

B. Uma[a], K. Sakthi Murugesan[c], S. Krishnan[d], S. Jerome Das[b], B. Milton Boaz[c,*]

[a] Department of Physics, R. M. K. Engineering College, Kavaraipettai 601 206, India
[b] Department of Physics, Loyola College, Chennai 600 034, India
[c] PG and Research Department of Physics, Presidency College, Chennai 600 005, India
[d] Department of Physics, B.S. Abdur Rahman University, Chennai 600048, India

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ABSTRACT

Single crystals of 2-furoic acid were grown by slow evaporation method within a period of 5 weeks at room temperature. The grown crystal was subjected to single crystal X-ray diffraction, UV–vis-NIR analysis, dielectric and surface analysis. The band gap energy is also calculated from UV studies. Theoretical calculations for polarizability which are useful for device fabrication are also made using Clausius–Mosotti equation and Penn analysis and their results are compared.

1. Introduction

The design and synthesis of organic non-linear optical materials is still a dynamic area of contemporary materials research. It is because, they possess superior second and third order nonlinear optical properties compared to the inorganic materials. The advantage offered by organic crystals over inorganic systems includes high electronic susceptibility ($\chi^{(2)}$) through high molecular polarizability (β), fast response time, facile modification through standard synthetic methods and relative ease of device processing. The large non-linearities of certain organic compounds are due to extended π-conjugated systems as well as the presence of asymmetrical charge transfer processes [1]. Now-a-days they are highly recognized as the materials of the future, as their molecular nature along with versatility of synthetic chemistry is used to alter their structure in order to maximize the non-linear properties [2,3].

The properties of organic compounds can be tailored using molecular engineering and chemical synthesis [4]. The design of organic polar crystals for quadratic NLO applications is supported by the observation that organic molecules containing πe^- system of asymmetric electron donor and acceptor groups of highly polarizable entities in which the problems of transparency and crystal growth may arise from their molecular crystal packing [5]. The organic materials are the key elements for future photonic technologies. Photonic is the application of photons for storing information and image processing. They allow tuning of the chemical structure and properties for the desired non-linear optical effects [6]. They possess large structural diversity and the molecules have wide application in frequency conversion, optical switching, optical signal processing and high speed electro optic (E_0) modulators [7]. In view of the aforesaid extended technological applications, in the present work, single crystals of 2-furoic acid (2FA) have been grown by slow evaporation technique and their theoretical, optical, dielectric and surface analysis have been discussed in detail.

2. Results and discussion

2.1. Material synthesis and growth

Analar grade furoic acid was dissolved in 50 ml ethanol in unimolar ratio and the solution obtained is stirred well at room temperature using a temperature controlled magnetic stirrer to yield a homogenous mixture of solution. Then the solution is filtered using a Whatmann filter paper and was allowed to evaporate at room temperature. The solution is recrystallized several times in order to increase the purity of the crystal. Optically clear and good quality seed crystal is kept inside the purified saturated solution and the solution is allowed to evaporate at room temperature, which produces an improved optically high quality and better shaped crystals of dimensions 8 mm × 2 mm × 2 mm within a period of 30 days. The grown crystal shows plate-like structure with uniform growth in all directions.

* Corresponding author. Tel.: +91 44 28544894; fax: +91 44 28510732.
E-mail address: miltonboazcm@yahoo.co.in (B.M. Boaz).

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Table 1
Several theoritical parameters on 2FA crystals.

Parameters	Values
Plasma energy (eV)	15.9790
Penn gap (eV)	1.4292
Fermi energy (eV)	11.8647
Polarizability (cm^3)	
Penn analysis	3.26×10^{-23}
Clausius–Mossotti equation	3.27×10^{-23}

2.2. Single crystal X-ray diffraction

Single crystal X-ray diffraction analysis for the grown crystals has been carried out to identify the cell parameters using an ENRAF NONIUS CAD 4 automatic X-ray diffractometer. The calculated lattice parameters from X-ray diffraction are $a = 10.586$ Å, $b = 6.675$ Å, $c = 3.812$ Å, $\alpha = 84.43^\circ$, $\beta = 95.15^\circ$ and $\gamma = 106.575^\circ$. The crystal crystallizes to triclinic system with the space group $P\bar{1}$, which was very well agreement with that of the reported values [8]. The valence electron plasma energy, $\hbar\omega_p$ is given by,

$$\hbar\omega_p = 28.8\left(\frac{Z\rho}{M}\right)^{1/2} \quad (1)$$

where $Z = ((4 \times Z_C) + (6 \times Z_H) + (4 \times Z_O)) = 30$ is the total number of valence electrons, ρ is the density and M is the molecular weight of the grown crystal. Explicitly $\hbar\omega_p$ dependent Penn gap and the Fermi energy [9] and is given by,

$$E_p = \frac{\hbar\omega_p}{(\varepsilon_\infty - 1)^{1/2}} \quad (2)$$

and

$$E_F = 0.2948(\hbar\omega_p)^{4/3} \quad (3)$$

Polarizability, α is obtained using the relation [10].

$$\alpha = \left[\frac{(\hbar\omega_p)^2 S_0}{(\hbar\omega_p)^2 S_0 + 3E_p^2}\right] \times \frac{M}{\rho} \times 0.396 \times 10^{-24} \ \ cm^3 \quad (4)$$

where S_0 is a constant for a particular material which is given by

$$S_0 = 1 - \left[\frac{E_p}{4E_F}\right] + \frac{1}{3}\left[\frac{E_p}{4E_F}\right]^2 \quad (5)$$

The value of α so obtained agrees with the value calculated using Clausius–Mossotti equation which is given by,

$$\alpha = \frac{3M}{4\pi N_a \rho}\left(\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2}\right) \quad (6)$$

where all the symbols have their usual significance. All these calculated data for the grown crystal are presented in the Table 1.

2.3. Optical absorption studies

The optical absorption spectrum of the grown crystal was recorded in the wavelength region ranging from 200 to 2000 nm using VARIAN CARY 5E spectrophotometer and is depicted in Fig. 1. For optical fabrications, the crystal should be highly transparent in the considerable region of wavelength [11,12]. The UV cut off wavelength for the grown crystal was found to be at 240 nm which makes it as a potential material for device fabrication.

The optical absorption coefficient (α) was calculated using the following relation,

$$\alpha = \frac{1}{d}\log\left(\frac{1}{T}\right) \quad (7)$$

where T is the transmittance and d is the thickness of the crystal. As the consequence of direct band gap, the crystal under study has

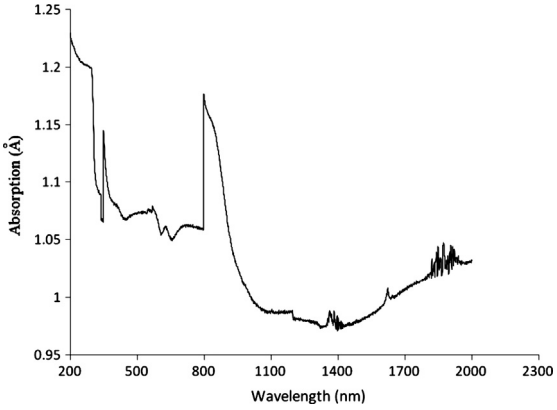

Fig. 1. UV spectrum of 2-furoic acid.

an absorption coefficient (α) obeying the following relation for high photon energies ($h\nu$):

$$\alpha = \frac{A(h\nu - E_g)^{1/2}}{h\nu} \quad (8)$$

where E_g is optical band gap of the crystal and A is a constant. The plot having the variation of $(\alpha h\nu)^2$ versus $h\nu$ is shown in the Fig. 2. The band gap evaluated from the graph is found to be 3.3 eV. As a result of wide band gap, the grown crystal has large transmittance in the visible region [13].

2.4. Dielectric measurements

Dielectric constant is one of the basic electrical properties of solids. Dielectric properties have also been correlated with electro-optic property of the crystals [14]. The capacitance (C_{crys}) and dielectric loss ($\tan\delta$) were measured using the conventional parallel plate capacitor method with frequency range (50 Hz to 5 MHz) using HIOKI – LCR HITESTER 3535 at various temperatures ranging from 313 to 323 K. The observations were also made while cooling the sample and the dielectric constant was evaluated by taking the average capacitance (C_{crys}). The variation of dielectric constant as a function of frequency is as shown in Fig. 3. The dielectric studies of 2FA crystals were performed by selecting high transparency rectangular shaped crystal plates of dimensions 4.75 mm × 2.5 mm × 1.5 mm and the sample is coated with good quality graphite to obtain a good conductive surface layer. In the observation it was found that there were sudden shoot-ups in dielectric constant (ε_r) at low frequencies (100 Hz).

The large value of dielectric constant at low frequency is due to the space charge polarization mechanism of molecular dipoles [15]. The dielectric permittivity of the crystal remains almost constant in the frequency range 400 Hz to 1 MHz. It was found that the dielectric constant is 45 at 5 MHz at 313 K. The dielectric constant in general decreases with increasing frequency for all temperatures. The dielectric constant of 2FA crystal at 323 K is 574 and this

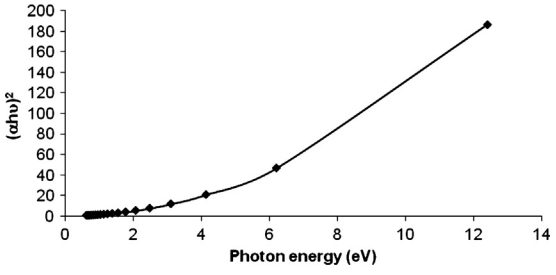

Fig. 2. Plot of $(\alpha h\nu)^2$ vs $(h\nu)$.