RESEARCH ARTICLE

Growth, Spectral, Optical, Electrical and Third Order Nonlinear Optical Properties of Organic Single Crystal: p-Toludinium Fumarate

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DOI: 10.5185/amp.2020.010388

p-Toludinium fumarate (PTF) a potential organic single crystal was grown by slow evaporation solution growth technique. Single crystal X-ray diffraction study was used to compute the unit cell parameters. The nuclear magnetic resonance spectral study reveals the proton and carbon molecular structure of PTF crystal. Optical band gap and the percentage of optical transmission were established by using UV-visible spectroscopy. Photoluminescence studies show that emission is independent of excitation wavelength. Dielectric constant (ε') and dielectric loss (tan δ) of PTF crystal were studied. The third order nonlinear refractive index (n_2) and third order nonlinear absorption coefficient (β) were estimated by Z-scan technique.

Introduction

Effort has been taken to synthesize and characterize the new molecules for nonlinear optical applications. Nonlinear optics is the technical restraint to understand the physical phenomena. Photonics technology utilizes photons instead of electrons to get, store, transmit and process information. Organic nonlinear crystals have played a vital role in nonlinear applications due to their large NLO coefficient and structure diversity, when compared to other inorganic counterparts. The molecules with π-conjugated electronic structures have been attracted due to their potential applications in optoelectronic and photonic devices [**1**]. The donor and acceptor group plays important role in determining the magnitude and optical efficiency of grown PTF crystal. p-Toluidine, a aryl amine has the chemical structure similar to aniline except that a methyl group is substituted onto the benzene ring. Fumaric acid is weak acid and it is one of two isomeric unsaturated dicarboxylic acids. The present investigation deals with growth and characterization of PTF crystal by single crystal X-ray diffraction, UV-Visible, photolumine-scence and NMR studies. The third order nonlinear optical studies have been performed by Z-scan technique.

Experimental procedure

Crystal growth

p-Toluidine (C_7H_9N) and Fumaric acid ($C_4H_4O_4$) were taken in equimolar ratio and the chemical reaction scheme of *p*-Toluidinium fumarate illustrated in **Fig. 1**. The estimated amount of the reactants was dissolved in double distilled water and solution was stirred for 6 hr. by using a magnetic stirrer to get homogenous concentration of solution. The purity of the synthesized salt was improved by successive recrystallization.A well-developed good transparent crystal of size 7×5×2 mm^3 was harvested in a growth period of 39 days as shown in **Fig. 2**.

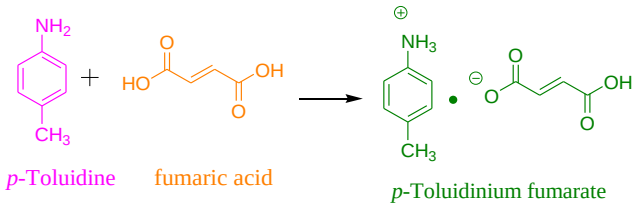

Fig. 1. Material synthesis scheme for *p*-Toluidinium fumarate.

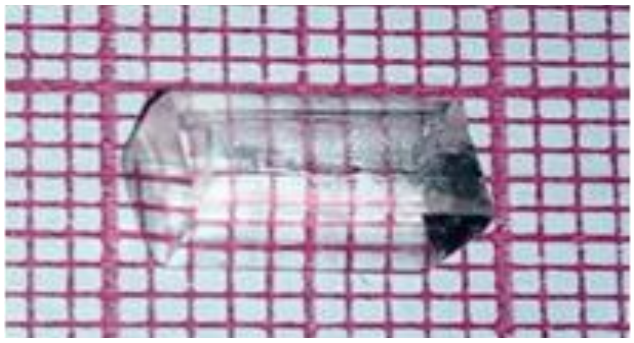

Fig. 2. Photograph of as grown PTF crystal.

Single crystal XRD analysis

Single crystal X-ray diffraction study was performed for PTF crystal and found that the grown crystal belongs to monoclinic system with centrosymmetric space group $P2_1/n$. The estimated lattice parameter values are a = 9.22 Å, b = 23.77 Å, c = 10.52 Å, α = γ = 90°, β = 94.48° and volume V = 2299 $Å^3$. These values are agreed very well with the reported data in the structural investigation [**2**].

UV-visible and photoluminescence spectral analysis

Fig. 2(a) shows the UV-visible spectrum of the grown PTF crystal. The cut-off wavelength of PTF crystal was found to be 285 nm which indicates that this material is a potential candidate for optoelectronic device. The band gap of the crystal was calculated by using the relation,

$$E_g = (1240/\lambda)\,\text{eV} \quad (1)$$

The band gap of the PTF crystal was found to be 4.2 eV. From the photoluminescence spectrum as shown in **Fig. 2(b)**, a broad emission peak observed at 420 nm with excitation wavelength 280 nm corresponds to violet emission of n → π* transition. It suggests that crystal can be used as violet light emitting diode.

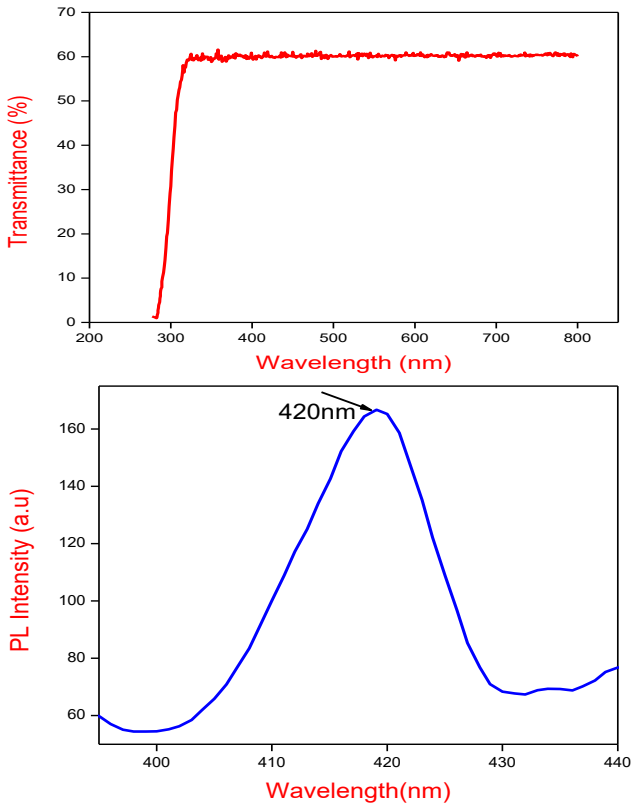

Fig. 2. (a) UV-Vis transmission spectrum of PTF crystal; (b) Emission spectrum of PTF crystal.

Nuclear magnetic resonance studies

The ^{1}H NMR and ^{13}C NMR spectra of *p*-Toludinium fumarate were recorded to confirm the carbon-hydrogen bonded network of the crystal. ^{1}H NMR spectrum of PTF crystal is shown in **Fig. 3**. The ^{1}H NMR spectrum of PTF compound reveals that –CH_3 proton appears as singlet at δ = 2.35 (s, 3H). It was observed that ArH aromatic protons appears as doublet at δ = 7.12-7.30 (d, 2H). The broad peak noted at δ = 9.81 is attributed to the protons in the amino functional group of the anilinium part of the complex [**3**]. The resonance peak corresponds to –CH groups of doublet noted at δ = 7.20 (d, 2H). The chemical shifts of ^{1}H NMR spectrum clearly confirm that, all the hydrogen atoms with respective environment present in molecular structure of the complex. The above mentioned results of proton NMR confirmed the molecular structure of PTF material.

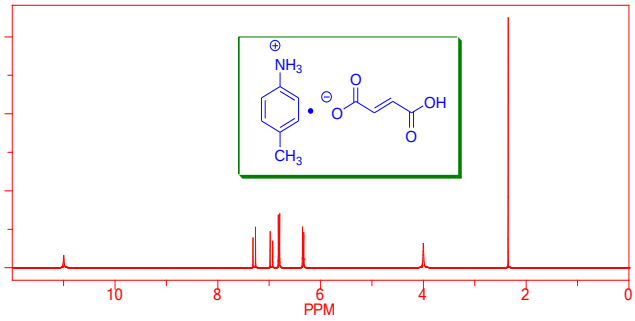

Fig. 3. ^{1}H NMR spectrum of PTF crystal.

In ^{13}C NMR spectrum, p-Toluidinium gives 5 signals and fumarate gives 2 signals which indicate that PTF has different chemical environmental with its carbon position as shown in **Fig. 4**.

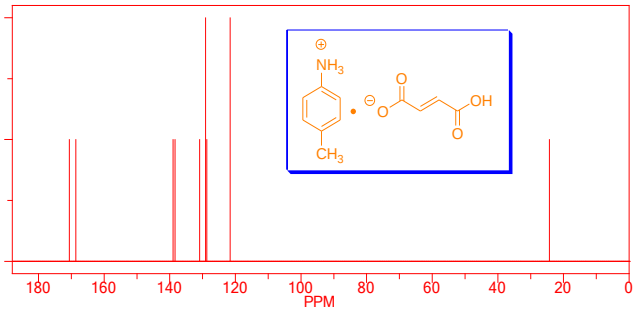

Fig. 4. ^{13}C NMR spectrum of PTF crystal.

Dielectric measurements

Dielectric constant (ε_r) and dielectric loss(tan δ) of the grown single crystal was measured as a function of frequency from 50 Hz to 3 MHz and these values were plotted with frequency at 303 K as depicted in **Fig. 5(a & b)**. The dielectric constant (ε_r) of the sample was calculated using the following relations,

$$\varepsilon_r = Ct/(\varepsilon_0 A) \quad (2)$$

$$\tan\delta = \varepsilon_r D \quad (3)$$

where C is the capacitance, t is the thickness of the crystal, ε_0 is the permittivity of free space, D is the dissipation factor and A is the area of PTF crystal. The dielectric constant were found to be higher at lower frequencies and slightly decreased at higher frequencies. This may be due to the contribution of all the four types of polarizations. At higher frequencies, the ionic and electronic polarizations are active [**4**].

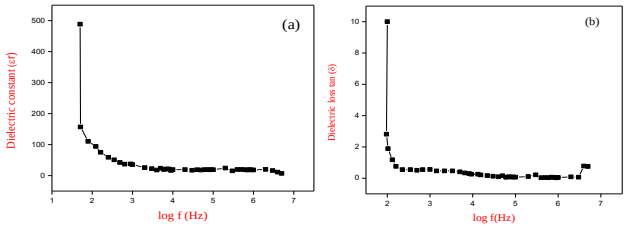

Fig. 5. (a) Plot of dielectric constant vs. log frequency of PTF crystal; (b) Dielectric loss vs. log frequency of PTF crystal.

Nonlinear optical study

Z-scan technique accomplished the third order nonlinear optical characteristics of PTF crystal. The sign and magnitude of the nonlinear refractive index (n_2) and the nonlinear absorption (β) was measured using open and closed configuration of Z-scan. The peak to valley configuration is an evidence for negative nonlinearity and is illustrated in **Fig. 6(a)**. This is also represented as self-defocusing effect which takes place due to the dependence of refractive index with temperature and finds application in the domain of fabricating optical sensors [**5**]. The open aperture configuration of Z-scan is displayed in **Fig. 6(b)**. The nonlinear absorption coefficient (β) was found to be 2.35×10^{-4}cm/W. It signifies the process of saturable absorption and widely useful for the application of optical power limiting process. The data obtained in this way reflects the effect of nonlinear refraction. The experimental measurement of n_2 and β allows one to determine the third order nonlinear optical susceptibility $\chi^{(3)}$. The determined values of nonlinear parameters n_2, β and $\chi^{(3)}$ of PTF crystal are -5.21×10^{-8} cm^2/W, 2.35×10^{-4}cm/W and 7.63×10^{-6}esu respectively.

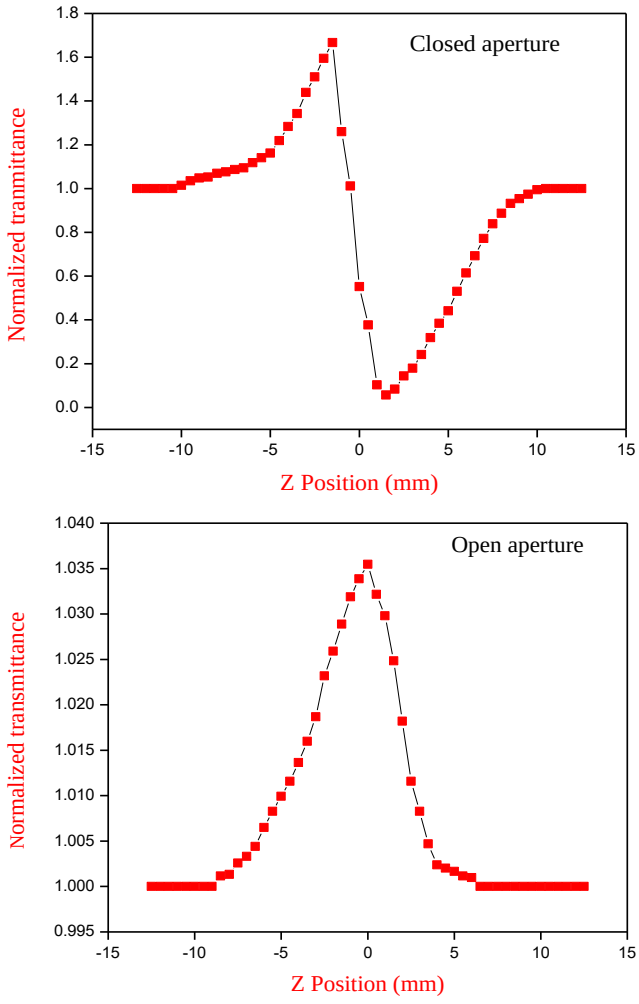

Fig. 6. (a) Closed aperture mode of PTF crystal; (b) Open aperture mode of PTF crystal.

The nonlinear absorption can be attributed to saturation absorption process, while the nonlinear refraction leads to self-defocusing in the compound. The Z-scan data precisely illustrates that PTF possess the third order nonlinear optical characteristics and it is suitable for optical limiting application.

Conclusion

Single crystal of PTF was grown by slow evaporation technique. The single crystal XRD analysis, UV-Vis transmittance studies and band gap energy estimation of the grown crystal were performed. The emission peak was observed from the photoluminescence spectral studies. Chemical constructions of the PTF crystal have been confirmed by NMR spectrum analysis. The low dielectric constant and dielectric loss of the PTF crystal showed the normal behavior at room temperature. The third order nonlinear optical parameters like refractive index (n_2), absorption coefficient (β) and susceptibility ($\chi^{(3)}$) were estimated by Z-scan technique. Thus, the various characterization of PTF crystal proved its suitability for optoelectronic device fabrication.

Keywords

Crystal growth, X-ray diffraction, nuclear magnetic resonance, dielectric constant, nonlinear optical material.

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