Growth and Characterization of p-Toluidinium Oxalate Organic Single Crystal for Nonlinear Optical Studies

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Abstract. Organic single crystal of p-Toluidinium oxalate (PTO) was grown by slow evaporation technique. Single crystal X-ray diffraction analysis reveals that PTO crystal belongs to monoclinic system with space group C2/c. The optical transmission study revealed the transparency of the grown crystal in the entire visible region and the cut off wavelength was found to be 222 nm. Photoluminescence spectral studies revealed the photon excitation. The presence of various functional groups in the grown crystal was identified from FTIR spectral analysis. The nonlinear refractive index (n_2) and nonlinear absorption coefficient (β) and third order nonlinear optical susceptibility were evaluated by Z-scan technique.

INTRODUCTION

Organic materials are attracting a great deal for the possible use in the fabrication of optical devices because of their large optical nonlinearity. The amplitude, phase modulation, laser technology, optical switching and other signal processing devices. The main advantage of organic materials is that they can be modified and tuned with respect to their chemical structure and properties. The design and synthesis of organic molecules exhibiting NLO properties have been motivated for their applications in the fast developing domains of optoelectronics and photonic technologies [1]. Extensive research in the last decades has shown that organic crystals often possess a higher degree of optical nonlinearity than their inorganic counterparts. p-Toluidine is aryl amine whose chemical structure are similar to aniline except that a methyl group is substituted onto the benzene ring. In many dicarboxylic salts an oxalic acid forms crystalline oxalate or with various organic molecules through hydrogen bonding interaction [2]. The present investigation deals with growth and characterization of PTO crystals by single crystal X-ray diffraction, UV-Visible, photoluminescence and FTIR studies. The third order nonlinear optical studies have been performed to understand the nonlinear optical properties of PTO crystal which are most useful for optical device applications.

GROWTH OF PTO CRYSTAL

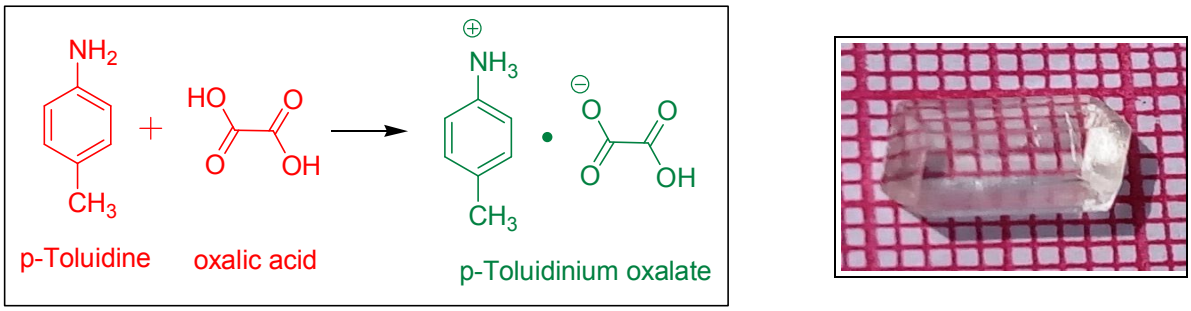
p-Toluidine (C_7H_9N) and oxalic acid ($C_2H_2O_4$) were taken in equimolar ratio and the chemical reaction scheme of p-Toluidinium oxalate was taken as illustrated in Fig.1(a). The estimated amounts of the reactants were dissolved in double distilled water and solution was stirred for 6 hr by using 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 $7\times5\times2$ mm^3 was harvested in a growth period of 38 days as shown in Fig.1 (b).

RESULTS AND DISCUSSION

Single crystal X-ray diffraction

Single crystal X-ray diffraction study was performed for PTO crystal and found that the grown crystal belongs to

monoclinic system with centrosymmetric space group C2/c. The estimated lattice parameter values are a = 26.567 Å, b = 5.702 Å, c = 13.942 Å, α = γ = 90°, β = 111.613° and volume V = 1309.8Å^3. These values are agreed very well with the reported data in the structural investigation [3].



(a) (b)

FIGURE 1.(a) Material synthesis scheme of p-Toluidinium oxalate, (b) Photograph of as grown PTO crystal

UV-visible analysis and Photoluminescence spectral analysis

UV-visible spectrum Fig. 2(a) shows that PTO crystal has a very lower cut-off wavelength around 222 nm with transparency around 60%. The band gap of the crystal was found to be 5.4 eV by using the relation,

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

The band gap and transmittance in the entire visible region enables the grown crystal is suitable for optoelectronic and photonics applications. From the Photoluminescence spectrum as shown in Fig. 2(b), a broad emission peak observed at 340 nm corresponds to ultraviolet emission of n → π* transition. It suggests that crystal can be used as a new ultraviolet light emitting diode.

(a) (b)

FIGURE 2.(a) UV-Vis transmission spectrum, (b) Photoluminescence spectrum of PTO crystal

FT-IR SPECTRAL ANALYSIS

FTIR spectrum of PTO crystal was recorded in the range 4000 – 400 cm^{-1} using KBr pellet technique and the presence of various functional groups in the grown PTO has been elucidated as shown in Fig. 3. The functional groups of PTO such as asymmetric and symmetric stretchings of N-H in the amino (NH_3^+) observed at the wave numbers 3496 and 3313 cm^{-1} respectively. The presence of methyl groups confirmed through the symmetric stretching and asymmetric bending of C-H at 2921 and 1419 cm^{-1} respectively. The C=C stretching for vibration of

were observed at 1683 and 1501 cm^{-1}. The peak observed at 1346 cm^{-1} was assigned to O-H in plane bending. The C-O stretching vibration was observed at 1245 cm^{-1}. O-H out of bending mode was observed at 750 cm^{-1} and 708 cm^{-1} [4]. Hence, the coordination of amine and carboxylic compounds are confirmed by the presence of prominent functional groups in the FTIR spectrum.

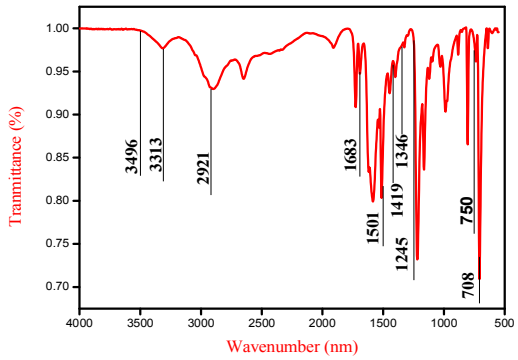
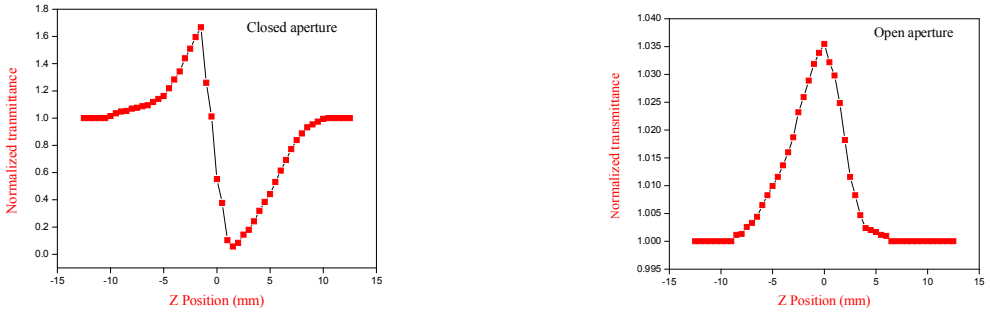


FIGURE 3. FTIR spectrum of PTO crystal

Z - scan measurement

The third order nonlinear optical characteristics of PTO were accomplished by means of the process of Z-scan. It is observed that the closed aperture Z-scan curve of PTO discloses the peak to valley configuration as well as it is an evidence for negative nonlinearity as illustrated in Fig. 4(a). The open aperture configuration of Z-scan is displayed in Fig. 4(b). The nonlinear absorption coefficient (β) was found to be 0.35 x 10-4cm/W. It signifies the process of saturable absorption and it is widely used for the application of optical power limiting process [5]. The data obtained in this way reflects the effect of nonlinear refraction. The experimental measurement of n_2 and β allow one to determine the third order nonlinear optical susceptibility $\chi^{(3)}$. The determined values of nonlinear parameters of PTO crystal are $n_2 = -9.32 \times 10\text{-}8cm^2/W$, $\beta = 0.35 \times 10^{-4}cm/W$ and $\chi^{(3)} = 7.83 \times 10^{-6}$ esu respectively. It indicates that PTO crystal exhibits nonlinear optical properties. Both β and n_2 contribute to the third order nonlinearity of the sample. It is shown that the nonlinear absorption can be attributed to saturation absorption process, while the nonlinear refraction leads to self-defocusing in the compound. Hence, PTO crystal is suitable for nonlinear optical applications such as the protection of human eyes and photo sensors [6].



(a) (b)

FIGURE 4. (a) Z-scan curve traced in closed aperture, (b) Z-scan curve traced in open aperture mode for PTO crystal

The Z-scan data precisely illustrates that PTO possess the third order nonlinear optical characteristics and enumerated in Table 1.

TABLE 1. Third order nonlinear parameters of PTO crystal

Sample	n_2 (cm^2W) $\times 10^{-8}$	β (cmW) $\times 10^{-4}$	Re $\chi^{(3)}$ (e.s.u) $\times 10^{-6}$	Im $\chi^{(3)}$ (e.s.u) $\times 10^{-6}$	$\chi^{(3)}$ (e.s.u) $\times 10^{-6}$
PTO	**-9.31**	**0.36**	**7.84**	**4.52**	**7.83**

CONCLUSION

Optical quality single crystal of p-Toluidinium oxalate was grown by slow evaporation technique. Single crystal X-ray diffraction studies confirmed the unit cell parameters and possessed monoclinic crystal structure. Optical transmission studies show that the crystal is transparent in the visible region with the cut-off 222 nm and hence it is suitable for frequency conversion applications. The various functional groups and the modes of vibrations were identified by FTIR studies. The third order nonlinear optical parameters like refractive index (n_2), absorption coefficient (β) and susceptibility ($\chi^{(3)}$) were estimated by the single beam Z-scan technique. The various characterization of PTO crystal proved its suitability for the future photonic and optoelectronic device fabrication.

REFERENCES

1. T. Thilaka, M. B. Ahameda, G. Vinitha, J. Opt. **124**, 4716-4720 (2013).
2. K. Balasubramanian, A. Ponchitra, J. Chem. Pharm. Sci. **9**, 129-131 (2016).
3. H. Thakuria, B. Moni Borah, A. Pramanik, G. Das, Chem. Crystallogr. **37**, 807-816 (2007).
4. A. Ponchitra, K. Balasubramanian, K. Muthu Sorna Meena, Int. J. Sci. Eng. Manag. **2**, 160-162 (2017).
5. M. Nageshwari, C. Rathika Thaya Kumari, G. Vinitha, M. Peer Mohamed, S. Sudha, M. Lydia Caroline, J. Mol. Struct. **1155**, 101-109 (2017).
6. M. Saravanan, T. C. S. Girisun, Mater. Chem. Phys. **160**, 413-419 (2015).