

# Spectroscopic Studies on Organic Nonlinear Optical Crystal : Enrofloxacinium Oxalate

D. Joseph Edison <sup>1</sup>, W. Nirmala <sup>2</sup>

<sup>1</sup>Department of Physics, St. Joseph's College of Engineering and Technology, Thanjavur, Tamil Nadu, India

<sup>2</sup>Department of Physics, Government Arts College, Tiruchirappalli, Tamil Nadu, India

## ABSTRACT

Organic nonlinear optical crystals of enrofloxacinium oxalate (EFO) was grown by slow evaporation technique at room temperature. The optical behavior was assessed by UV-Vis analysis and it was found with no absorption in the visible region and it may be useful for second harmonic and other relevant applications. The existences of various functional groups were identified using FT-IR spectroscopic study ranging between 4000 and 400 cm<sup>-1</sup>. Thermo gravimetric and differential scanning analyses were employed to analyze the thermal stability of the crystal. <sup>1</sup>H-NMR spectrum was taken to elucidate the environment of carbon and hydrogen in the proposed crystal. EFO crystal was further subjected to second harmonic generation (SHG) test to confirm nonlinear property.

**Keywords:** EFO, FT-IR, NMR, SHG, Organic Crystal

## I. INTRODUCTION

In the recent scenario, the significant research attention has been paid to nonlinear optical materials due to their enormous application in the area of telecommunication, photonics, optoelectronics and optical storage devices [1-3]. Organic nonlinear crystals are gaining attention because they have high flexibility in terms of molecular structure, high optical damage threshold, low cost and short response time to optical excitation [4-7]. Many of the organic molecules are substituted with  $\pi$  electron donors and accepters which exhibits intermolecular charge transfer resulting in high SHG efficiency [8, 9]. Electronic transition in the UV- Visible region improves the NLO efficiency to satisfy the needs of technological development. Many investigations are being carried out to synthesize new organic material with high SHG efficiency. In this present work, single crystal of enrofloxacinium oxalate (EFO) have been grown by slow evaporation technique. EFO was further characterized by FT-IR, UV-Vis-NIR, FT-NMR and

thermal analyses. The Kurtz and Perry powder technique confirms the NLO property of the grown crystal.

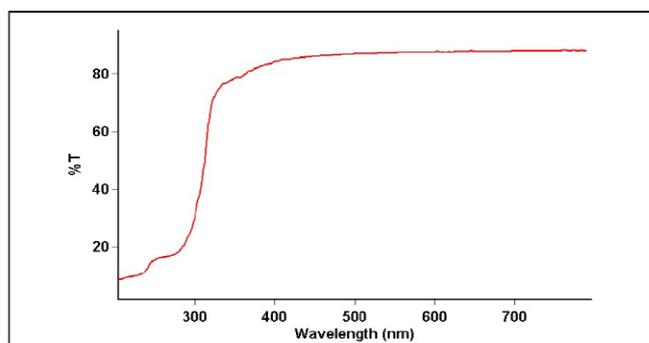
## II. Experiment

Enrofloxacinium oxalate has been crystallized from the mutual solution of enrofloxacin and oxalic acid in ambient conditions. The stoichiometric amount of component salts were thoroughly dissolved in acetonitrile and dimethyl sulfoxide and mixed using a magnetic stirrer. The mixture was evaporated by slow evaporation in a temperature controlled water bath to avoid any possible decomposition. The synthesized colorless crystalline sample of EFO was obtained. The synthesized compound was further purified by the repeated recrystallization procedure.

### III. Result and Discussion

#### 3.1. UV-Vis-NIR spectral analysis

The optical transmission spectrum of EFO was recorded by UV-VIS-NIR spectrophotometer Varian Cary 5000 is shown in Fig. 1.

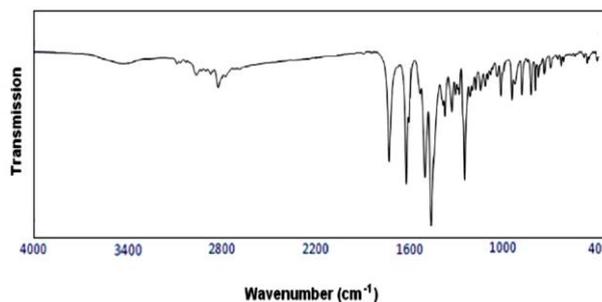


**Figure 1.** Transmission Spectrum of EFO.

The recorded transmission spectrum of grown crystal shows that EFO is optically transparent in the wavelength region 200-800 nm. The transmittance nature of the crystal is found to be in the entire visible region. From the spectrum, it is evident that lower cut off wavelength is 300 nm [10]. It is observed from the transmission spectrum that absorption band range between 210-250 nm are due to  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  transitions [11].

#### 3.2. FT-IR Analysis

The Fourier transform infra-red analysis (FT-IR) of EFO crystal was recorded in the range 400-4000  $\text{cm}^{-1}$  employing a Perkin Elmer FT-IR spectrophotometer by KBr pellet method to identify the functional groups present in the grown crystal. Fig. 2. shows the IR profile of EFO crystal and Table 1 shows the functional group assignments.



**Figure 2.** FT-IR Spectrum of EFO.

The strong absorption at 1712  $\text{cm}^{-1}$  is due to the presence of COOH and COO<sup>-</sup> groups of the compound and it confirms the reaction of oxalic acid with enrofloxacin [12, 13]. The asymmetric mode of NH<sub>3</sub><sup>+</sup> group vibration occurred at 1608  $\text{cm}^{-1}$ . The presence of asymmetric and symmetric stretching mode of the CH<sub>3</sub> group was identified with its deformation modes at 1566  $\text{cm}^{-1}$  and 1304  $\text{cm}^{-1}$  respectively.

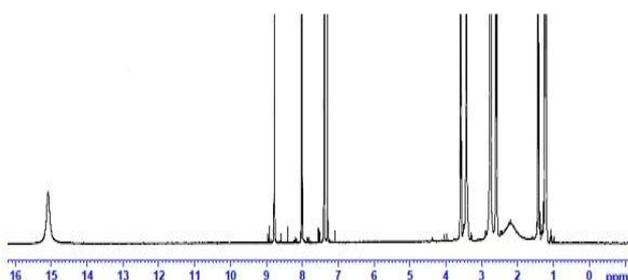
Wavenumber ( $\text{cm}^{-1}$ )	Assignment
1712	COO <sup>-</sup> symmetric stretching
1608	NH <sub>3</sub> <sup>+</sup> symmetric stretching
1566	CH <sub>3</sub> asymmetric stretching
1486	CH wagging
1413	COO <sup>-</sup> symmetric stretching
1304	CH <sub>3</sub> symmetric stretching
1250	C-COO <sup>-</sup> symmetric stretching

**Table 1.** FT-IR assignment of EFO.

The peak at 1486  $\text{cm}^{-1}$  corresponded to aromatic CH wagging [14]. Absorption at 1413  $\text{cm}^{-1}$  corresponds to the symmetric stretching of COO<sup>-</sup>. A strong absorption arising from C-COO<sup>-</sup> symmetric stretching was observed at 1250  $\text{cm}^{-1}$  [15].

### 3.3. Nuclear Magnetic Resonance study

Nuclear magnetic resonance (NMR) is a very versatile technique employed in the identification of organic compounds [16]. The  $^1\text{H}$ -NMR spectrum of EFO have recorded using  $\text{D}_2\text{O}$  as solvent on a Bruker 300MHz (Ultrasield)TM instrument at  $23^\circ\text{C}$  (300MHz for  $^1\text{H}$ -NMR) to confirm the molecular structure. The obtained spectrum is shown in Fig. 3.



**Figure 3.**  $^1\text{H}$ -NMR Spectrum of EFO.

The chemical shifts are tabulated in Table 2. From the spectrum, it is observed that in the region at  $\delta=1.215$ - $1.442$  ppm confirm the disparition of these peaks and probably the cleavage of the piperazine cycle followed by the formation of NH function.

**Table 2.** Chemical Shift of EFO.

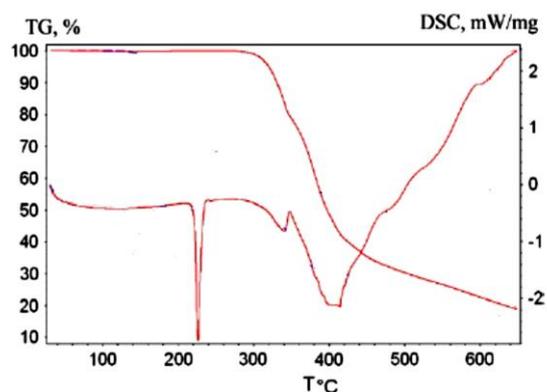
Spectra	Chemical Shift (ppm)	Group identification
$^1\text{H}$ NMR	1.78	- CH <sub>3</sub> -
	3.45	- CH <sub>2</sub> -
	4.69	- D <sub>2</sub> O
	8.01	- CH-
	15.12	COOH

The methyl proton signal is split into multiplet due to the coupling of neighbouring (-CH<sub>3</sub>-) proton which is

confirmed from the signal at  $\delta = 1.783$  ppm. The doublet signal observed at  $\delta = 3.45$  ppm is attributed to ( $\text{CH}_2$ ) proton next to carboxylic acid. The signal at  $\delta = 4.69$  ppm is due to the solvent  $\text{D}_2\text{O}$ . The signal at  $\delta = 8.019$  ppm is due to aromatic CH group. It is found that the characteristic signal of  $-\text{COOH}$  group, which lies at the values 15.12 ppm with less intensity. This peak is justified that the coordination of enrofloxacin with oxalic acid via the carboxylic group [17].

### 3.4. Thermal analysis

The Thermo Gravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC) spectra of EFO crystal have been obtained using the instrument NETSZCH SDT Q 600 V8.3 Build 101. The initial mass of the material for the analysis was 2.9240 gms. The TGA and DSC have been carried out in nitrogen atmosphere at a heating rate of  $20^\circ\text{C}/\text{min}$  from  $20^\circ\text{C}$  to  $600^\circ\text{C}$ . The TGA and DSC curve are presented in Fig. 4.



**Figure 4.** TGA / DSC Trace of EFO.

The TGA trace shows that the material exhibit small weight loss of about 3.07 % in the temperature range  $79^\circ\text{C}$  to  $208^\circ\text{C}$  due to loss of lattice water. There is a major weight loss of about 85.53 % that occurs between  $323^\circ\text{C}$  to  $500^\circ\text{C}$  due to decomposition of EFO compound and it shows that decomposition is almost completed. The DSC trace indicates that a sharp

endothermic peak at 323 °C. It exactly coincides with the decomposition observed in TGA/DSC trace. It reveals that the crystal is thermally stable up to 323 °C and EFO crystal is suitable for NLO application up to 323°C.

### 3.5. Second Harmonic Generation test

The nonlinear optical susceptibility of EFO crystals were measured through second harmonic generation test using standard Kurtz and Perry method [18]. The powdered sample is placed in the path of Nd:YAG laser with pulse width of 8 ns and repetition rate 10 Hz. The intensity of incident power is 3.5 mJ / pulse. A tight packing of powder samples was ensured with aid of mechanical vibrator. The capillary tubes were placed 3 cm away from the focal point to avoid laser induced damage in sample. The output, could be seen as a bright green flash emission, was congregated by a monochromator towards the photomultiplier tube. The green color output signals from the sample confirmed the second harmonic generation. The intensity of output light was observed as 12 mV.

## IV. CONCLUSION

Transparent single crystals of enrofloxacinium oxalate were grown from aqueous solution in room temperature using slow evaporation technique. Optical transmission studies confirm that the grown crystal is transparent in the entire visible region and there is no absorption of light. The presence of all the fundamental functional groups of the grown sample was confirmed by FT-IR analysis. The <sup>1</sup>H-NMR analyses confirm the molecular structure of the grown crystal. The thermal analyses indicate that the crystal can be placed for any application below 323 °C. From the study by Kurtz and

Perry technique, the proposed crystal can be a potential NLO material.

## V. ACKNOWLEDGEMENT

Authors would like to express their grateful to St. Joseph's College, Trichy, for recording the FTIR spectrum. The authors thank Dr. P.K. Das, Indian Institute of Science, Bangalore, India for providing SHG facilities. The authors acknowledge SASTRA University, Thanjavur, India for NMR spectral facilities. The authors are very much grateful to electro chemical research Institute, Karaikudi, India for thermal analysis.

## VI. REFERENCES

- [1]. D. Wang, G. Zhou, X. XU, X. Wang, H. Liu, Y. Ren, Z. Shao, M. Jiang, *Opt. Laser Technol.* 34 (2002) 343- 346.
- [2]. X.Q. Wang, D. Xu, X.F. Cheng, M.K. LU, D.R. Yuan, Growth morphology and properties of the organometallic nonlinear optical crystal MnHg(SCN)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>• 2C<sub>4</sub>H<sub>9</sub>NO, *Phys. Status Solidi A* 198 (2003), 43- 48.
- [3]. J. Erwann, A. Nathalie, D. Xerox, *J. Mater. Chem.* 12 (2002) 2383-2389.
- [4]. S.R. Marder, J.W. Perry, *Molecular materials for second-order nonlinear optical applications*, *Adv. Mater.* 5 (1993) 804-815.
- [5]. P. Tanusri, K. Tanusree, B. Gabriele. R. Lara, *Synthesis, Growth, and Characterization of L-Arginine Acetate Crystal: A Potential NLO Material*, *Cryst. Growth Des.* 3 (2003) 13-16.
- [6]. I. Ledoux, J. Badan, J. Zyss, A. Migus, D. Hulin, J. Etchepare, G. Grillon, A. Antonetti and B. Josa, *Generation of high-peak-power tunable infrared femtosecond pulses in an organic crystal:*

- application to time resolution of weak infrared signals, *J. Opt. Soc. Am. B* 4 (1987) 987.
- [7]. S. Boomadevi, H.P. Mittal and R. Dhansekar, "Synthesis, Crystal Growth and Characterization of 3-Methyl 4-Nitropyridine 1-Oxide (POM) Single Crystals," *Journal of Crystal Growth*, Vol. 261, No. 1, 2004, pp. 55-62. *Journal of Crystal Growth* 261 (2004) 55.
- [8]. F. Yogam, I. Vetha Potheher, M. Vimalan, R. Jeyasekaran, T. Rajesh Kumar, P. Sagayaraj, Growth and physicochemical properties of 1-phenylalaninium maleate: A novel nonlinear optical crystal *Spectrochim. Acta A* 95 (2012) 369-373.
- [9]. B. Zhao, C. Chen, Z. Zhou, Y. Cao, M. Li, A comparative study on the nonlinear optical properties of diphenyl ether and diphenyl sulfide compounds, *J. Matter Chem.* 10 (2000) 1581-1584.
- [10]. W.H. EI Shwiniy, M.S EI Attar, S.A. Sadeek, *J. Korean Chemical Society* 57 (2013) 52 - 62.
- [11]. E.K. Ethimiadou, H. Thomasdaki, Y. Sanakis, C.P. Raptopoulou, N. Katsaros, A. Scorilas, A. Karaliota, G. Psomas, *J. Inorg Biochem*, 101 (2007) 64-73.
- [12]. J. Mohan, *Organic spectroscopy principles and Applications*. Narose Publishing Housen New Delhi, 2005.
- [13]. R.S. Krishnan, V.K. Sankaranaryanan, K.J. Krishnan, *Raman And Infra - Red Spectra Of Amino Acids*, *J. Ind. Inst. Sci* 55 (1973), 66.
- [14]. A.R. Gargaro, L.D. Barron and L. Hecht, Vibrational Raman optical activity of simple amino acids, *J. Raman Spectrosc.* 24 (1993) 91.
- [15]. B.D. Mistry, *A Handbook of spectroscopic Data*. ADB Publishers, 2000.
- [16]. P.Y. Bruice, *Organic Chemistry*, Pearson Education Pvt. Ltd, New Delhi, 2002.
- [17]. S.A. Sadeek, W.H. EI Shwiniy, M.S EI Attar, *Spectrochim. Acta A* 84 (2011) 99-104.
- [18]. S.K. Kurtz, T.T. Perry, A Powder Technique for the Evaluation of Nonlinear Optical Materials, *J. Appl. Physics* 39 (1968) 3798-3813.