NON-LINEAR OPTICAL PROPERTIES OF TRIS THIOUREA POTASSIUM CHLORIDE SINGLE CRYSTALS

[1] Dr.Jini pramila M, [2]Dr.Gegi G Vb

[1]Assistant Professor, Department of Physics, Loyola Institute of Technology and Science, Thovalai, Kanyakumari, Tamilnadu, India.

[2]Assistant Professor, Department of Chemistry, Loyola Institute of Technology and Science, Thovalai, Kanyakumari, Tamilnadu, India.

Abstract : *An organic nonlinear optical crystal of tris thiourea potassium chloride has been grown by slow evaporation technique. The optical absorption study reveals that the grown TTPC crystal exhibit lower cut off wavelength at 300 nm and the minimum band tail (urbach) energy indicates the good crystalline nature of TTPC crystal. The non-linear optical (NLO) parameters are theoretically calculated by the DFT method. Non-linear optical properties were also estimated with the aid of a TTPC molecule as a model of an acceptor, and a final set of optimal systems were identified as potential candidates to be implemented as photovoltaic material. The above essential parameters manifest appropriate usage of TTPC as a nonlinear optical material.*

Keywords: NLO; Urbach energy.

1.INTRODUCTION

Nonlinear optics (NLO) is the branch of optics that describes the behavior of light in non-linear media in which the dielectric polarization responds nonlinearly to the electric field of the light. The nonlinearity is only observed at very high light intensities such as those provided by pulsed lasers. The coherent radiation at a few discrete frequencies can be produced by laser devices as in solid-state lasers or with narrow range of tenability as in dye lasers. The nonlinear optical properties give the detailed information about the important aspect of the matter, because the nonlinear optical activity mainly depend on the electronic and vibrational structure, inter and intra molecular structure of the molecules [1]. The origin of the nonlinear optics effect was first investigated by Franken et al., 1961 with the discovery of second harmonic generation (SHG) in quartz crystal shortly after the demonstration of the first working laser by Maiman 1960. Thereafter, various new nonlinear optical phenomena have been discovered to develop the nonlinear response [2]. At present NLO activity of a material plays a remarkable role in the multidimensional fields like telecommunication, industry, medicine, remote sensing, optical data storage, optical signal processing, optical computers, ultrafast switches, ultra-short pulsed lasers, sensors, laser amplifiers [3] and so on. Apart from the SHG, there are other nonlinear optical effects, optical parametric oscillation, acousto-optic effect, self-focusing of light, and simulated Raman scattering [4]. Nowadays,

ultimate NLO materials gained great importance in most of the practical oriented applications of Science and Technology.

2. EXPERIMENTAL DETAILS

Thiourea and potassium chloride was purchased from the Sigma Aldrich company with 98% purity and used without purification. The slow evaporation method was used to grow the single crystals at room temperature. Optically transparent crystals were obtained by spontaneous nucleation from the saturated solution. The UV-visible spectrum of TTPC was examined in the range 190-900 nm using CARY 100 B10 UV-visible spectrophotometer in $CdCl_3$ solvent. The spectral measurements were carried out at a sophisticated analysis instrumentation facility (SAIF), IIT Madras, Chennai.

3. COMPUTATIONAL DETAILS

The Gaussian 09W program package was used to perform DFT calculations at the B3LYP/6-31 G(d,p) to analyze the non linear optical properties of TTPC [5].

4. RESULT AND DISCUSSION

4.1 Crystal growth

Thiourea and Potassium chloride compound was purchased from Sigma-Aldrich company with a stated purity of 98% and was recrystallized. The given compound was dissolved in distilled water, thoroughly mixed using a magnetic stirrer (4 h) at room temperature to obtain a homogeneous solution. The solution was tightly covered with a perforated polythene sheet in a glass beaker and kept at constant temperature. Numerous tiny crystals were formed at the bottom of the beaker due to spontaneous nucleation. Transparent colorless crystals of TTPC were harvested in a period of 25–30 days. Photograph of the grown TTPC crystal is shown in Fig.1
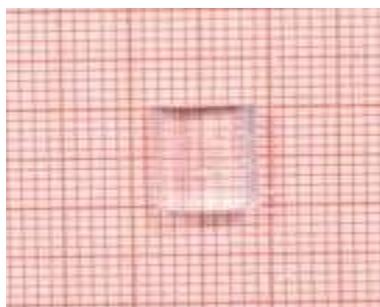

Fig.1 Photographs of grown TTPC single crystal

The grown TTPC crystal was subjected to single crystal XRD analysis. The calculated lattice parameters a = $7.565A^0$, b = $7.254A^0$, c = $6.69A^0$ and β = 376.8^0.

4.2 Optical Studies

Optical characterization is a vital parameter to be considered for good quality check of crystalline materials. The optical transmission range and transparency cutoff wavelength of the TTPC are important factors for optical applications. The UV-visible transmittance study of TTPC exemplifies the linear optical properties. UV-visible spectral analysis gives information about the electronic transition of the compound [6]. Also, it would help to understand the electronic structure and the optical band gap of the crystal. Here, the UV spectrum shows less absorption between 300-900nm, which reflects the presence of wide transparent window in the entire visible region. The high transmittance property is attributed to the good optical quality and defect free volume of the crystal. At lower wavelengths, the optical transmission is discontinued in the ultraviolet region due to absorption of energy which arises from the valence band to unfilled conduction band. In Fig.2, a strong absorption with a fall of transmittance at 300nm shows the lower cutoff wavelength of the title compound. Absorption bands observed in the region from 300-900nm is attributed to intramolecular charge transfer transitions among the marginal donor group and acceptor group core [7]. Sufficiently, low cutoff wavelength and wide transparency window of a crystal suggest good optical quality.
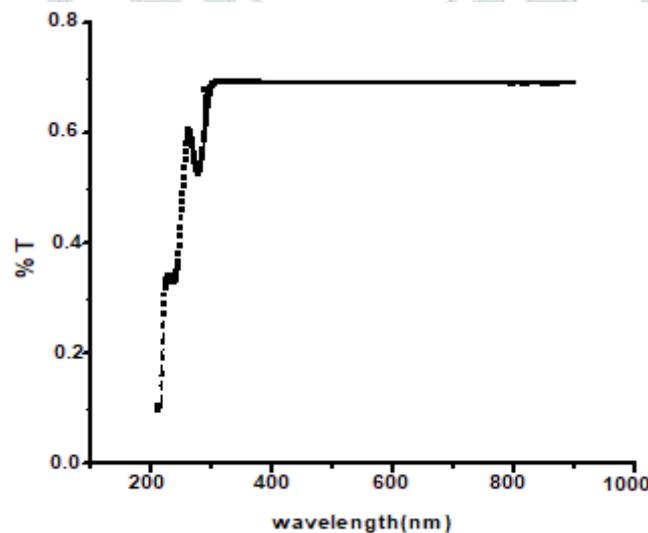

Fig.2. UV-vis Transmission spectrum of TTPC

The optical band gap (E_g) has been evaluated from the transmission spectra and the optical absorption coefficient(α) near the absorption edge is given by

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

where A is a constant, E_g the optical band gap, h the planck's constant and ν the frequency of incident photons. The electronic band gap energy of TTPC crystal was evaluated. The band gap was found to be 4.10eV. The wide band gap of the TTPC crystals supports the requirement for the good quality nonlinear optical applications [8].

4.3 NON-LINEAR OPTICAL PROPERTIES (NLO)

Nonlinear optical (NLO) materials create new electromagnetic field by changing properties such as frequency and phase of the radiation. These materials, which are effective in photonic signal processing, are a source of interest for a large number of technological applications for optical communication and computing, optical switching and limitation, data storage and recovery and dynamic image processing [9]. The polarity, first and second hyperpolarizability properties of the molecular system were calculated using the DFT/B3LYP/6-31 G (d,p) method.

The isotropic mean polarizability $\langle\alpha\rangle$, anisotropy of the polarizability ($\Delta\alpha$) and the total dipole moment (μ) are calculated using the following equations.

$$\alpha_0 = \tag{1}$$

$$\Delta\alpha = [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2]^{1/2} \tag{2}$$

the second harmonic generation first-order hyperpolarizability $\beta(-2\omega;\omega, \omega)$ can be calculated using the x, y, z components

$$\beta = ((\beta_{xxx}+\beta_{yyy}+\beta_{zzz})^2+(\beta_{yyy}+\beta_{yzz}+\beta_{yxx})^2+(\beta_{zzz}+\beta_{zxx}+\beta_{zyy})^2)^{1/2} \tag{3}$$

The components of dipole moment, polarizability, first order hyperpolarizability and second order hyperpolarizability of TTPC were estimated. The calculated value of total static dipole moment μ, the average linear polarizability α_0, the anisotropy of the polarizability $\Delta\alpha$ and the first hyperpolarizability β are 1.019 Debye, 21.521×10^{-24} esu, 30.524×10^{-30} esu, 6.214×10^{-30} esu, respectively. The β value of TTPC has been compared with the β value of urea (0.3728×10^{-30} esu) which is a standard reference material. This large β value (more than 16 times larger than urea) indicates the potential of TTPC to exhibit second order optical effect [10].

The third-order response by second-order hyperpolarizability offers effective and richer behaviour than the second-order NLO response due to the higher dimensionality of the frequency space. The equation for average second hyperpolarizability is

$$\tag{4}$$

The second order hyperpolarizability is found to be 64.258×10^{-36} esu. The higher values of dipole moment, molecular polarizability and hyperpolarizabilities are important for NLO applications[11]. So, we can conclude that, due to low band gap energy which has been explained in UV and high γ, β and μ, TTPC can have industrial application in the form of NLO material.

5. CONCLUSION

Single crystals of TTPC have been recrystallized by slow evaporation solution growth technique at room temperature. Optical absorption studies depict the transparency of the crystal in the entire visible

region which in turn highlights the nature of the material for nonlinear optical device fabrication and the cutoff wavelength was found to be 300 nm and the energy gap value of the grown crystal is 4.10 eV. The first and second hyperpolarizability value calculated was about 6.214×10^{-30} esu and 64.258×10^{-36} esu. The calculated values were compared with non-linear optical material urea, the title compound was 16 times higher. The high value of first and second hyperpolarizability shows that the title compound can be used as a new material in non-linear optical studies. The outcome of all these results authenticated that the NLO response, good thermal stability and wide optical transparency of TTPC crystal is a kind of excellent material for photonics and optoelectronic device application.

REFERENCES

[1] M.Manikandan, P.Rajesh, P.Rajaswamy, Crystal growth, structural, optical, vibrational analysis, Hirshfeld surface and quantum chemical calculations of 1, 3, 5-triphenyl benzene single crystal, J. Mol.Struct. 1195 (2019) 659-669.

[2] G.Parvathy, R.Kaliammal, V.Kousalya Devi, A.Nivedhitha Bharathy, G.Vinitha, K.Sangaranarayanan, S.Sudhahar, Experimental and theoretical evaluation of a novel organic proton transfer crystal p-Toluidinium 5-chloro-2-hydroxy benzoate for third order nonlinear optical applications, Chinese Journal of Physics 75(2022) 76-89.

[3] R.Rajakumar, P.Praveen Kumar, Structure, crystal growth and characterization of piperazinium bis (4-nitrobenzoate) dehydrate crystal for nonlinear optics and optical limiting applications, J.Mol.Struct. 1179 (2019) 108-119.

[4] B.K.Sarojinia, B. Narayanab, B.V.Ashalathab, J. Indirac, K.G. Lobo, Synthesis, crystal growth and studies on non-linear optical property of new chalcones, 295 (2006) 54–59.

[5] M.J. Frisch, Gaussian 09W program, Gaussian Inc., Wallingford, C.T, 2009.

[6] Hiral Raval, P.S.Raval, B.B.Parekh, M.J.Joshi., Growth, experimental and theoretical analysis of physical properties of an organic NLO 2Methylimidaole L-Tartrate (2MILT) crystal, J. of Physics and chemistry of solids., 156 (2021) 109908.

[7] J. Tauc, A. Menth, and D. L.Wood, "Optical and Magnetic Investigations of the Localized States in Semiconducting Glasses," Physical Review Letters, vol. 25, no. 11, pp. 749–752, 1970.

[8] D. Jacquemin, E.A. Perpe'te, I. Ciofini, C. Adamo, R. Valero, Y. Zhao, D.G. Truhlar, On the performances of the M06 family of density functionals for electronic excitation energies, J. Chem. Theory Comput. 6 (2010) 2071–2085.

[9] Mahmood A. Albo Hay Allah, Asim A. Balakit, Hamida Idan Salman,Ali Ahmed Abdulridha, Yusuf Sert, New Heterocyclic Compound as Carbon Steel Corrosion Inhibitor in 1 M H2SO4, High Efficiency at Low Concentration: Experimental and Theoretical Studies, Journal of Adhesion Science and Technology,

[10] Aysha Fatima, Ghazala Khanum, Arun Sharma, Km Garima, Sandhya Savita, Indresh Verma, Nazia Siddiqui, Saleem Javed, Computational, spectroscopic, Hirshfeld surface, electronic state and molecular docking on phthalic anhydride, J. of Mol. Struc., 1249 (2022) 131571.

[11] G.Rajasekar, G.Maheshwaran, N.Swarna Sowmya, A.Bhaskaran, R.Mohan Kumar, S.Jayavijayan, M.Krishna Kumar, S.Sudhakar, Studies of crystal growth, structural, spectral, and optical properties of solution grown 2-phenylethylaminium p-nitrophenolate monohydrate single crystals for efficient nonlinear optical applications, J. Mol. Struct. 1225 (2021) 129304.