STUDIES ON THE DIELECTRIC PROPERTIES OF ORGANIC 3,5-DINITROBENZOICACID-4-AMINOACETOPHENONE SINGLE CRYSTALS FOR OPTICAL APPLICATIONS

T.R. Anitha[1], T. Suthan[2,*], C. Gnanasambandam[3], P.P. Abirami Priya[4]

Abstract

The organic compound 3,5-dinitrobenzoicacid-4-aminoacetophenone has been synthesized and single crystals were grown successfully by slow evaporation technique using acetone solvent at room temperature. The powder X-ray diffraction study reveals the crystalline nature of the synthesized compound. The FTIR spectral analysis is used to identify the various functional groups present in the grown crystal. The thermal behaviour of the grown crystal has been investigated using Thermogravimetric (TG) and Differential Thermal analyses (DTA). The dielectric studies of the grown crystal have been performed by using conventional parallel plate capacitor method. The variation of dielectric parameters such as dielectric constant, dielectric loss and ac conductivity as a function of temperature and frequency has been studied.

Keywords: single crystal; powder X-ray diffraction; FTIR; TG/DTA; Dielectric

[1]Research Scholar (Reg. No:18223152132023), Department of Physics, S.T. Hindu College, Nagercoil – 629002, Tamil Nadu, India (Affiliated to Manonmaniam Sundaranar University, Tirunelveli – 627012, Tamil Nadu, India)
[2*]Assistant Professor, Department of Physics, Lekshmipuram College of Arts and Science, Neyyoor – 629802, India
[3]Associate Professor, Department of Physics, S.T. Hindu College, Nagercoil – 629002, India
[4]Biomeitez Research and Development Pvt. Ltd, Saral, Kanyakumari – 629203, India

***Corresponding Author:** T. Suthan
*Assistant Professor, Department of Physics, Lekshmipuram College of Arts and Science, Neyyoor – 629802, India

DOI: - 10.53555/ecb/2021.10.4.32

1. Introduction

The synthesis of novel organic materials with potential nonlinear optical properties induced active research in the growth of high quality single crystals towards technological applications. The merits of organic materials are their large optical susceptibilities, lower cut off wavelengths and a wide optical transparency window in the visible region. The prominent NLO properties of organic compounds are due to the presence of delocalized π electron-conjugated systems. The structure of the organic materials can be modified to optimize its nonlinear optical properties. The high NLO properties of organic materials make them excellent for device fabrication in optical limiting and information processing. Organic single crystals find applications in the manufacture of LEDs, organic solar cells, organic field effect transistors etc [1-8]. Hence an attempt has been made to synthesis novel organic compound from benzoic acid and acetophenone family with optimistic nonlinear optical property. In the present work, an organic compound 3,5-dinitrobenzoic acid-4-aminoacetophenone has been synthesized and single crystals have been grown by slow evaporation method. The grown crystals have been characterized by powder XRD, FTIR, thermal and dielectric studies.

2. Experiment

The commercially available AR grade organic compounds namely 3,5-dinitrobenzoic acid and 4-aminoacetophenone were used for the crystal growth process. The 3,5-dinitrobenzoic acid is an organic non-hygroscopic compound. It has a molecular formula of $C_7H_4N_2O_6$ and molecular weight of 212.12 g/mol. The non-hygroscopic organic compound 4-aminoacetophenone has a molecular formula of C_8H_9NO and molecular weight of 135.16 g/mol. The raw materials 3,5-dinitrobenzoic acid and 4-aminoacetophenone were taken in the equimolar (1:1) ratio to synthesize the organic 3,5-dinitrobenzoic acid-4-aminoacetophenone compound. The calculated amount of the raw materials were taken in a beaker, dissolved in acetone solvent and stirred continuously for 3 hours using a magnetic stirrer to get a saturated solution. The solution was then filtered using Whatman filter paper to remove any impurities present in the solution. The filtered solution was then transferred into a beaker and closed with perforated polythene sheet for the slow evaporation of the solvent. Good quality single crystals of the synthesized compound 3,5-dinitrobenzoic acid-4-aminoacetophenone were harvested. The purity of the grown crystals was improved by repeated crystallization processes.

3. Result and Discussion

3.1 X-ray Diffraction analysis

The powder X-ray diffraction pattern of the finely crushed 3,5-dinitrobenzoicacid-4-aminoacetophenone single crystal was recorded using a XPERT-PRO diffractometer with CuKα(λ = 1.54056A˚) radiation at room temperature. The analysis was carried out in the scan range 10 to 70°. The obtained powder XRD pattern of the grown crystal is shown in Fig. 1. The observed sharp and high intense diffraction Bragg's peaks at the specific 2θ angle confirms that the grown 3,5-dinitrobenzoicacid-4-aminoacetophenone crystals have good crystalline quality.

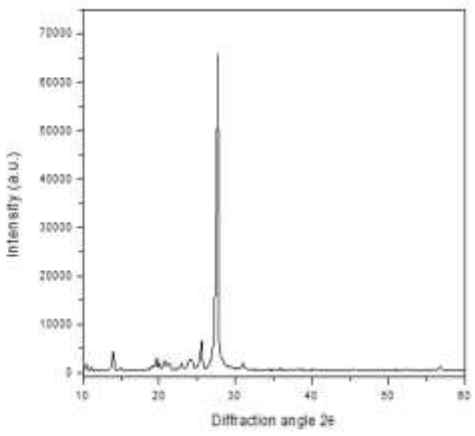

Fig. 1 Powder XRD pattern of 3,5-dinitrobenzoicacid-4-aminoacetophenone

3.2 FTIR spectral analysis

The Fourier Transform Infrared spectral analysis is performed to validate the various functional groups present in the grown 3,5-dinitrobenzoicacid-4-aminoacetophenone single crystal. The FTIR spectrum was recorded using a Perkin Elmer Spectrum Two FTIR spectrometer by the KBr pellet technique in the wavenumber region 4000–400 cm^{-1}. The obtained FTIR spectrum of the grown crystal is shown in Fig. 2. The IR absorption peaks observed at 3478 cm^{-1} and 3379 cm^{-1} correspond to asymmetric and symmetric stretching vibration of the primary aromatic NH_2 group. The aromatic =(C-H) stretching vibration is confirmed by the IR peak at 3096 cm^{-1}. The IR absorption peak at 2926 cm^{-1} is assigned to the C–H symmetric stretching vibration of the methyl group. The C=O stretching vibration of the carboxylic acid is characterized by the IR absorption peak at 1719 cm^{-1}. The aromatic ketone C=O stretching vibration is confirmed by the IR peak at 1643 cm^{-1}. The observed IR peak at 1598 cm^{-1} is attributed to the aromatic C=C stretching vibration. The IR absorption peak at 1536 cm^{-1} corresponds to the asymmetric stretching vibration of the aromatic NO_2 group. The methyl C– H bending vibration is characterized by the IR peak at 1445 cm^{-1}. The observed IR peak at 1347 cm^{-1} is assigned to the symmetric stretching vibration of the aromatic NO_2 group. The C–C–C stretching vibration of the aromatic ketone is confirmed by the IR absorption peak at 1273 cm^{-1}. The IR peak at 1175 cm^{-1} is attributed to the C– H in plane bending vibration of the benzene ring. The IR peak at 846 cm^{-1} corresponds to the nitroaromatic C–N stretching vibration. The C– H out-of-plane bending vibration of the benzene ring is characterized by the IR peak at 722 cm^{-1}. The IR absorption peak at 688 cm^{-1} is assigned to the aromatic O–H out-of-plane bending vibration [9-17].

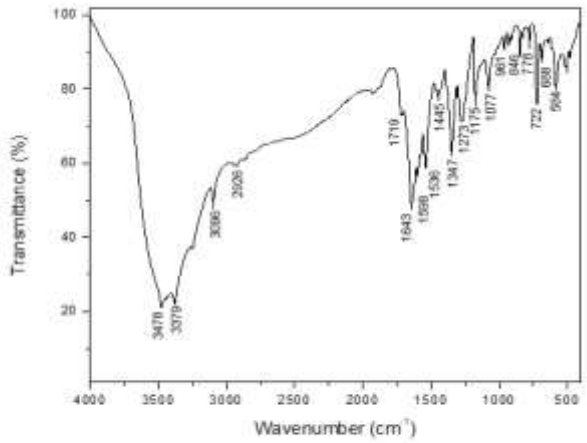

Fig. 2 FTIR spectrum of 3,5-dinitrobenzoicacid-4-aminoacetophenone

3.3 Thermal analysis

The thermal stability of the grown 3,5-dinitrobenzoicacid-4-aminoacetophenone single crystal was studied by simultaneous thermogravimetric and differential thermal analyses. The TG/DTA spectrum was recorded using Hitachi STA7300 instrument for the temperature range of 40°C to 760°C in the nitrogen atmosphere at a heating rate of 20°C/min. he obtained TG/DTA curve of the grown crystal is shown in Fig. 3. The TGA curve shows that the grown crystal is stable up to 214°C. In the DTA curve, the sharp endothermic peak observed at 129°C is assigned to the melting point of the grown crystal because there is no significant weight loss in the TGA curve at that temperature. It is also noticed from the TG/DTA curve that the grown crystal does not undergo any phase transition up to the melting point. The sharp endothermic peak in the DTA curve indicates the good crystalline nature of the title compound.

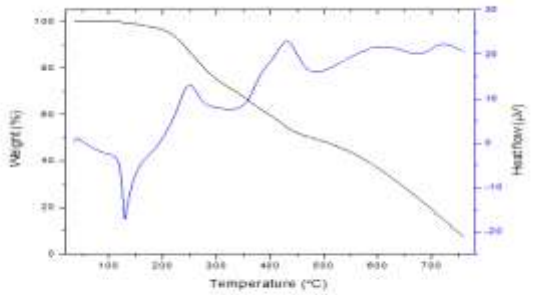

Fig.3 TG/DTA curve of 3,5-dinitrobenzoicacid-4-aminoacetophenone

Melting point, a characteristic property of solid crystalline materials, is used to identify and ascertain the purity of different materials. Organic crystals have weak intermolecular interaction forces with relatively low bonding energy resulting in low lattice energy. Hence, the melting and boiling points of organic crystals are very less compared to inorganic crystals. The larger organic molecules have higher melting points because the strength of the intermolecular interaction forces increase with the large number of atoms. The melting point of 3,5-dinitrobenzoicacid-4-aminoacetophenone has been compared with other reported organic single crystals and are listed in Table 1 [18-23].

Table 1: Comparison of melting point of 3,5-dinitrobenzoicacid-4-aminoacetophenone with other organic crystals

Organic crystal	**Melting point (°C)**	**Ref**
2-hydroxy-4-methoxybenzophenone	67	[18]
4-dimethylaminobenzaldehyde	76	[19]
3,4,5-trimethoxybenzaldehyde	80	[20]
Naphthalene	82	[21]
Benzil	96	[22]
4-nitrobenzaldehyde	107	[23]
3,5-dinitrobenzoicacid-4-aminoacetophenone	129	Present work

3.4 Dielectric studies

The dielectric study provides useful information about the electrical properties of the materials as a function of temperature and frequency. The dielectric behaviour of the grown 3,5-dinitrobenzoicacid-4-aminoacetophenone single crystal was analyzed by Agilent 4284A Precision LCR meter for various temperatures ranging from 313 K to 373 K. The measurements were carried out in the frequency range of 20 Hz – 1 MHz by using the conventional parallel plate capacitor method. The dielectric constant ε_r was evaluated from the measured capacitance values by using the following relation

$$\varepsilon_r = \left(\frac{1}{C_{air}}\right)\left(C_{crys} - C_{air}\left(1 - \frac{A_{crys}}{A_{air}}\right)\right)\left(\frac{A_{air}}{A_{cys}}\right)$$

where A_{crys} and A_{air} represent the crystal area and electrode area respectively. The ac electrical conductivity σ_{ac} of the grown crystal was determined as follows

$$\sigma_{ac} = \varepsilon_0 \varepsilon_r \omega \tan\delta$$

where ε_0 the permittivity of free space, ω the angular frequency and tan δ the dielectric loss factor. The variation of dielectric constant, dielectric loss and ac conductivity as a function of temperature and frequency are plotted in the Fig. 4(a-c). It is noticed that as the temperature increases, the dielectric constant, dielectric loss and ac conductivity value increases. It is also observed that as the frequency increases, the dielectric constant and dielectric loss factor value decreases but the ac conductivity increases. This indicates the normal dielectric behaviour of the grown 3,5-dinitrobenzoicacid-4-aminoacetophenone crystal. At low frequency, the dielectric constant value was relatively higher

because of the role of all the polarization mechanisms namely, electronic, ionic, orientation and space charge polarization. But at high frequency, the dielectric constant value gets decreased because of the significant loss of the polarization mechanisms. The low dielectric constant and dielectric loss value at high frequency reveals the good optical quality of the grown crystal with lesser defects. This is an important criterion for material's photonic and nonlinear optical applications [24, 25].

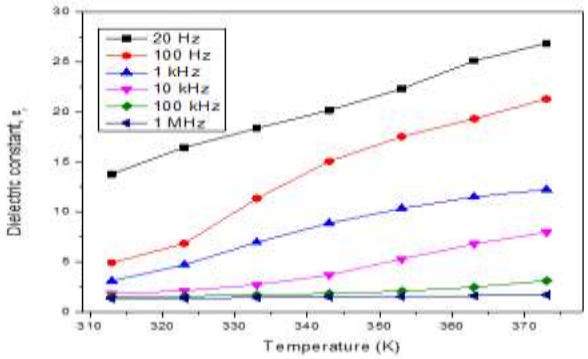

Fig. 4(a) Temperature and frequency dependent dielectric constant

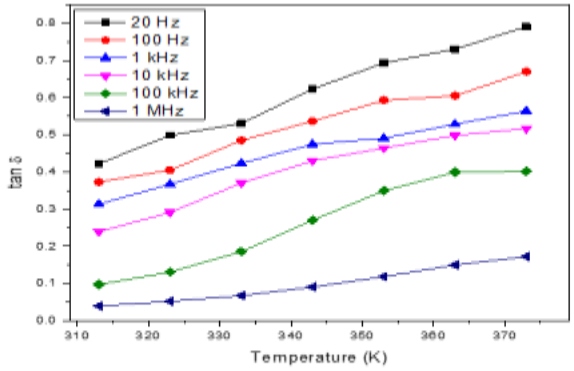

Fig. 4(b) Temperature and frequency dependent dielectric loss

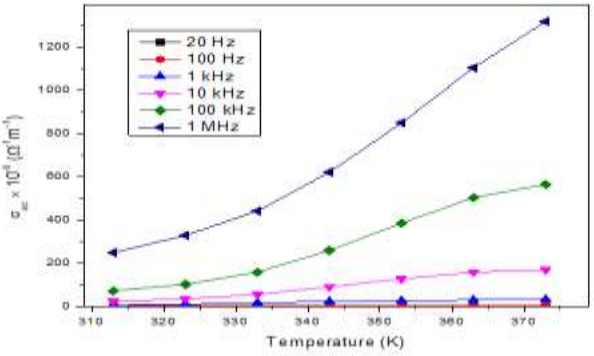

Fig. 4(c) Temperature and frequency dependent ac conductivity

The activation energy of the grown crystal was determined by using the Arrhenius plot as shown below

$$\sigma_{ac} = \sigma_0 exp\left(\frac{-E_a}{kT}\right)$$

where σ_{ac} indicates the ac electrical conductivity at any temperature T, σ_0 denotes the pre-exponential factor, E_a indicates the activation energy, k is the Boltzmann constant and T the absolute temperature [26]. The above equation can take the form as shown below

$$\ln \sigma_{ac} = \ln \sigma_0 - \left(\frac{E_a}{kT}\right)$$

The plot between ln σ_{ac} and1000/T was drawn in the frequency range 20 Hz – 1 MHz which is shown in Fig. 4(d). The slope of the Arrhenius plot is used to calculate the activation energy of the grown crystal. The frequency dependence of activation energy is presented in Fig. 4(e). It is noted that the activation energy decreases with the increase in frequency. This is due to the hopping transport mechanism of the charge carriers under the influence of the applied electric field frequency [27].

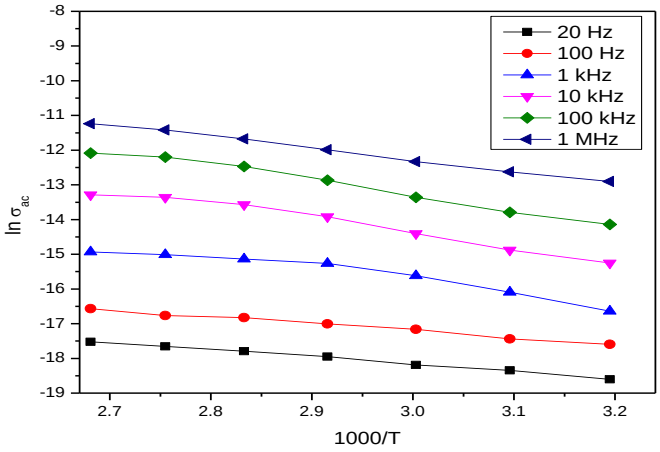

Fig. 4(d) Plot of ln σ_{ac} versus 1000/T for various frequencies

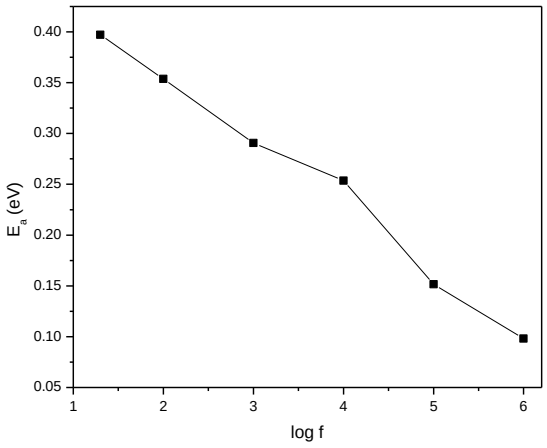

Fig. 4(e) Frequency dependence of activation energy

4. Conclusion

The organic compound 3,5-dinitrobenzoicacid-4-aminoacetophenone was synthesized and single crystals were grown by slow evaporation solution growth technique from acetone solvent at room temperature. The crystalline nature of the synthesized compound was confirmed by powder XRD analysis. The FTIR spectral analysis was carried out to confirm the various functional groups present in the grown crystal. The thermal stability of the grown crystal was investigated using TG/DTA spectral analysis. The DTA curve showed the melting point of the grown crystal as 129°C. The melting point of the grown crystal was compared with other reported organic crystals. The variation of the dielectric parameters such as

dielectric constant, dielectric loss and ac conductivity as a function of temperature and frequency was analyzed. The grown 3,5-dinitrobenzoicacid-4-aminoacetophenone organic crystal had shown normal dielectric behaviour.

References

1. Mohd. Shkir, Haider Abbas, Spectrochim Acta A Mol Biomol Spectrosc 125 (2014) 453-457
2. S. Siva Bala Solanki, N.P. Rajesh, T. Suthan, Opt. Laser Technol. 93 (2017) 143–148
3. DS Chemla, J Zyss, Nonlinear Optical Properties of Organic Molecules and Crystals, Academic Press, Orlando, New York (1987)
4. S. Nandhini, K. Sudhakar, S. Muniyappan, P. Murugakoothan, Mater. Today: Proc., 8 (2019) 256-263
5. T. Suthan, N.P. Rajesh, C.K. Mahadevan, K. Senthil Kumar, G. Bhagavannarayana, Spectrochim. Acta A. 79 (2011) 1443–1448
6. T. Suthan, N.P. Rajesh, C.K. Mahadevan, G. Bhagavannarayana, Mater. Chem. Phys. 129 (2011) 433–438
7. R.W. Munn, C.N. Ironside, Principles and Applications of Nonlinear Optical Materials, First Edition, Chapman & Hall, London (1993)
8. T. Suthan, N.P. Rajesh, C.K. Mahadevan, D. Sajan, G. Bhagavannarayana, Mater. Chem. Phys. 130 (2011) 915–920.
9. Lynnette Joseph, D. Sajan, K. Chaitanya, T. Suthan, N.P. Rajesh, Jayakumary Isac, Spectrochim Acta A Mol Biomol Spectrosc. 120 (2014) 216–227
10. Robert M. Silverstein, Francis X. Webster, David J. Kiemle, Spectrometric Identification of Organic Compounds, Seventh Edition, John Wiley & Sons, Inc., New Jersey (2005)
11. Peter J. Larkin, IR and Raman Spectroscopy - Principles and Spectral Interpretation, Elsevier Inc., Oxford (2011).
12. D. Sajan, K. Chaitanya, K. Safakath, Reji Philip, T. Suthan, N.P. Rajesh, Spectrochim Acta A Mol Biomol Spectrosc. 106 (2013) 253–261
13. Donald L. Pavia, Gary M. Lampman, George S. Kriz, James R. Vyvyan, Introduction to Spectroscopy, Fifth Edition, Cengage Learning, Stamford, CT (2013)
14. Ewen Smith, Geoffrey Dent, Modern Raman Spectroscopy – A Practical Approach, John Wiley & Sons, Ltd., England (2005)
15. D. Sajan, I. Hubert Joe, V.S. Jayakumar, J. Raman Spectrosc. 37 (2006) 508-519
16. M.K. Subramanian, P.M. Anbarasan, V. Ilangovan, S. Moorthy Babu, Spectrochim. Acta A 71 (2008) 59-67
17. B.S. Arun Sasi, R.P. Jebin, T. Suthan, C. James, J. Mol. Struct. 1146 (2017) 797-807
18. T. Suthan, N.P. Rajesh, C.K. Mahadevan, G. Bhagavannarayana, Spectrochim. Acta A 78 (2011) 771–776
19. R.P. Jebin, T. Suthan, N.P. Rajesh, G. Vinitha, U. Madhusoodhanan, Spectrochim Acta A Mol Biomol Spectrosc. 135 (2015) 959–964
20. R.P. Jebin, T. Suthan, N.P. Rajesh, G. Vinitha, Optics and Laser Technology 115 (2019) 500–507
21. T. Suthan, N.P. Rajesh, P.V. Dhanaraj, C.K. Mahadevan, Spectrochim Acta A Mol Biomol Spectrosc. 75 (2010) 69-73
22. T. Suthan, P.V. Dhanaraj, N.P. Rajesh, C.K. Mahadevan, G. Bhagavannarayana, CrystEngComm. 13 (2011) 4018-4024
23. T. Suthan, N.P. Rajesh, J. Cyst. Growth, 312 (2010) 3156-3160
24. T. Suthan, P.V. Dhanaraj, N.P. Rajesh, Spectrochim. Acta A 87 (2012) 194–198
25. Tomoyuki Akutagawa., Sadamu Takeda., Tatsuo Hasegawa., Takayoshi Nakamura., J. Am.Chem. Soc. 126 (2004) 291–294
26. S. Karuppusamy, K. Dinesh Babu, V. Nirmal Kumar, R. Gopalakrishnan, Appl. Phys. A 122 (2016) 498
27. Fahrettin Yakuphanoglu, Ertan Evin, Mustafa Okutan, Physica B 382 (2006) 285-289