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The Importance of Thermal Stability and Phase Transition Studies for Novel Organic Materials in Concern of Device Applications

D. Haleshappa[1,*], Jayarama A[2], Abdul Rahiman[3], L.S.Prasad[3]
[1]Assistant professor, Department of Physics, Yenepoya Institute of Technology, Moodbidri, Karnataka, India
[2]Professor, Department of Physics, Alva's Institute of Engineering and Technology, Moodbidri, Karnataka, India
[3]Assistant professor, Department of Mechanical Engineering, Yenepoya Institute of Technology, Moodbidri, Karnataka, India

ABSTRACT

A novel chalcone derivative (E) 1-(furan-2-yl)-3-(4-nitrophenyl) prop-2-en-1-one (2AF4N) has been synthesized and crystallized using slow evaporation solution method. The grown single crystals were characterized by Fourier transform infrared vibrational technique. The spectroscopic investigations confirmed the presence of various functional groups in the grown single crystals. The 2AF4N crystals possess high optical transmittance beyond cut-off wavelength in the entire visible region. The energy band gap of the material is found using Tauc's plot and by a direct method. The thermal stability of the crystals has been examined by TG/DTA/DSC measurements. The 2AF4N crystals are thermally stable up to 224 ^{0}C. The thermal stability and optical transparency of the novel organic materials reveals the credibility in nonlinear optical applications.

Keywords: *Phase transition, Thermal stability, Single crystal*

****Corresponding Author***
E-mail: halesh.phy@gmail.com

INTRODUCTION

Over past fifty years, a great deal of research has been performed in the field of nonlinear optics along with new nonlinear optical phenomena and various contemporary applications [1]. The nonlinear optical materials particularly organic crystals gain attention in recent years related to several potential applications in modern optical data storage, optical limiting, telecommunication, laser frequency conversion, holographic imaging, and so on[2-4]. The selection of material for nonlinear optical (NLO) applications depends on their physical and optical properties such as high melting point, thermal stability, and wide optical transparency. Also, organic nonlinear optical materials are attracting a great deal of attention, as they have large optical susceptibilities, inherent ultrafast response, and high optical thresholds for laser power as compared with inorganic materials [5-7]. In this context, the organic chalcone materials are most advisable because their structure can be easily tailored to enhance their optical nonlinearity as a consequence of the delocalization of ‘π’ electrons in the structure [7]. Subsequently the search for appropriate novel organic NLO materials exhibiting an ensemble of optical and functional properties never ceased. Therefore last two decades a large number of D-π-A type molecules were designed [8]. Among them, furan is one of the most extensively employed electron rich material for these systems being their excellent thermal stability, wide optical transparency in the visible region, semiconducting nature, photo physical and photo chemical property, good environmental stability [9]. Taking these theoretical features in mind, currently many furan based chalcone derivatives like (2E)-1-(1-benzofuran-2-yl)-3-(2-bromophenyl) prop-2-en-1-one [10], (E)-1-(2-furyl)-3-(X)prop-2-en-1-one (IIIa-IIIc) [11] are reported for nonlinear optical applications. It is also reported that bromo, methoxy, and nitro substitution in the benzene moiety plays a major role in varying nonlinear efficiency [12]. In addition to this our research group has spread the attention on better NLO efficiency material than the earlier reported materials. Meanwhile, literature survey suggests that the donor substituted materials gives a major contribution in enhancing the NLO property due to the strong delocalization of electrons over a π-bridge [13]. Moreover, the chalcone molecules with a π-conjugated system that provides a large charge transfer axis. Among many other substituents nitro group seems to be a better candidate for the substitution due to their push-pull behavior in the molecular axis. Since, nitro substitution in furan based chalcone leads to the formation donor–π–acceptor (D–π–A) type chalcone derivative with better nonlinear optical efficiency, a novel nitro substituted push-pull type chalcone derivative; (E) 1-(furan-2-yl)-3-(4-nitrophenyl) prop-2-en-1-one (2AF4N) has been synthesized and characterized using various spectroscopic studies. In the current report, thermal, and linear optical properties of a novel (E) 1- (furan-2-yl)-3-(4-nitrophenyl) prop-2-en-1-one (2AF4N) derivative has been carried out.

EXPERIMENTAL PROCEDURE

The (E) 1-(furan-2-yl)-3-(4-nitrophenyl) prop-2-en-1-one (2AF4N) compound was synthesized using Claisen-schimidt condensation reaction and single crystals were grown by adapting slow solution evaporation technique [14]. A 2-acetyl furan (0.01mol) and 4 nitro benzaldehyde (0.01mol) were blended in 40 ml of ethanol and stirred for one hour at ambient temperature. Then the resulting product was poured in to the cold water and the isolated raw product was filtered and washed with sterilized water and dried to obtain the organic chalcone material. The synthesized compound was dissolved in 50 ml acetone and the saturated solution was filtered to remove the unwanted suspended entities in the solution. The saturated solution in a beaker was kept for nucleation with tight covering at room temperature. After 15 days a tiny nucleated single crystals were observed which are allowed to grow further up to experimental size using slow evaporation method [15].

CHARACTERIZATION

The synthesized chalcone derivative is characterized to confirm the functional groups in the sample using FTIR vibrational spectroscopic method. The FT-IR vibrational spectrum was obtained using thermo Nicolet, Avatar 370 spectrometer in the measurement range 4000 - 400 cm^{-1} with KBr pellet method [11]. The recorded FTIR Spectra of 2AF4N is shown in Figure 1.

The thermal reviews like material stability, good crystallinity, and sample purity were analysed for the 2AF4N sample through thermal analysis. The data for thermal analysis was obtained using simultaneous TGA/DSC SDT Q600 V20.9 Build 20 thermal analyser under nitrogen gas flow with a heating rate of 10 ^{0}C min^{-1} on 5.907mg sample in the temperature range between 25 °C and 600 °C. The thermal behaviour and stability of the crystal was analysed by thermogravimetric/differential thermal analysis/differential scanning calorimetry measurements with a sample weight 5.907mg. The simultaneous TG/DTA/DSC curve of 2AF4N crystal is shown in Figure 2.

The linear optical properties have been analysed with the help of UV-Vis-NIR spectrum. The spectral data was collected for the sample using Shimadzu 1800 UV-Vis-NIR spectrophotometer in dimethylformamide solution (0.01mol) in the wavelength range 200 -1100 nm at room temperature.

RESULTS AND DISCUSSIONS

The recorded FTIR Spectra of 2AF4N is shown in Figure 1. The characteristic peaks in the FTIR spectra at vibrational frequency 3113 and 2924 cm^{-1} are attributed to aromatic C-H stretching vibrations. The vibrational band line at 1662 cm^{-1} in the spectra is due to C=O stretching vibrations. The characteristic peak around 1602 cm^{-1} is assigned to C=C stretching vibrations. The vibrational frequency at 1248 cm^{-1} in the spectra is corresponding to C-O stretching vibrations. In the present study, C-C-C in plane bending vibrations is observed in the spectra at 848 and 757 cm^{-1}. These respective vibrations in the FTIR spectra confirm the presence of functional groups in the synthesized chalcone derivative.

The simultaneous TG/DTA/DSC curve of 2AF4N crystal is shown in Figure 2. The sharp peak in the DSC curve shows good crystallinity and purity of the crystal. The smooth curve in DSC plot up to melting point is indicates the thermal stability of the crystal against thermal crack. The TGA curve shows that the mass of the sample remains unchanged till 123.24 °C after that a minor weight loss about 3.345% was noticed before the melting point due to dehydration. A major weight loss about 71.74% was observed in the TGA plot between 223- 288.8 °C and is due to the decomposition of the sample. The TGA curve illustrates that after heating the sample beyond 288.8 °C, the residual weight is approximately 18.01 % of the initial weight. The DTA curve of the 2AF4N crystal revealed that the sample undergoes an irreversible endothermic change at 224 °C is corresponding to the melting point of the sample and the same was also noticed in the DSC curve. There is no endothermic or exothermic peaks are appeared in the DSC/DTA curve after melting point. The thermal resistance of 2AT3N endures superior than that of standard urea (130 °C) [12] and don't get decomposed till the melting point. Thus, the analysis report suggests that the 2AF4N is the advisable material for NLO applications up to its melting temperature.

The absorbance in the UV region is very essential factor for an NLO crystal to be useful in NLO applications. The ultra violet –visible (UV-Visible) spectrum of the crystal was shown in Figure 3. The recorded spectrum reveals that the 2AF4N crystal has a wider transparency range extending into entire visible and infrared region and the absorption is noticed in the UV region at 319 nm this may be oriented in consequence n-π* transitions. [13].

The cut-off wavelength for the crystal 2AF4N is found to be 383 nm. The linear absorption coefficient (α) of the 2AT3N crystal was estimated from the absorbance data using the following equation,

$$\alpha = \frac{2.303\times Absorbance}{d} \qquad (1)$$

Where'd' is the thickness of the sample. The value of α helps to determine the optical band gap (E_g) of the crystal using Tauc's equation [14],

$$(\alpha h\vartheta) = \alpha_0\left(h\vartheta - E_g\right)^n \qquad (2)$$

Where, 'α' is the linear absorption coefficient, α_0 is the band edge constant that depends on the transition probability, 'hν' energy of the UV beam and 'n' is the index that characterizes the absorption process; theoretically the value of n can be given by ½ and 2 for direct and indirect band gap structure respectively. The direct band gap can be estimated by plotting a graph (hν) v/s $(\alpha h\vartheta)^2$ and shown in Figure 4. The band gap (E_g) can be determined from extrapolating the linear portion of the curve to a point $(\alpha h\vartheta)^2 = 0$ and the direct band gap value thus obtained is 3.54 eV. This graphical value of the direct band gap is very close to the energy band gap value obtained from the cut-off wavelength of the crystal using the relation, $E_g = {hc}/{\lambda_{cutoff}}$ (3.243 eV) [15,16]. Hence, the 2AF4N crystal can be a potential material for nonlinear optical device applications.

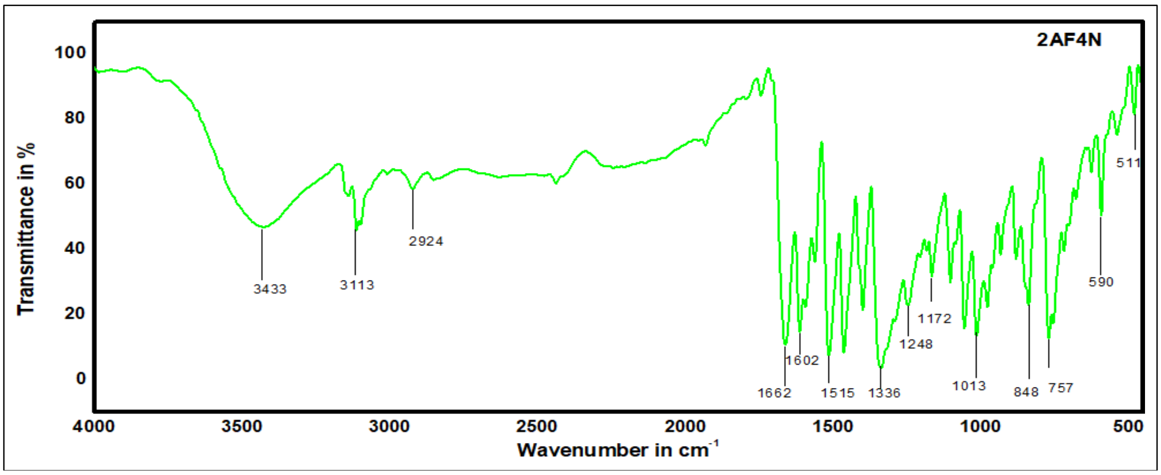

Fig. 1. *The FT-IR vibrational spectra of 2AF4N crystal*

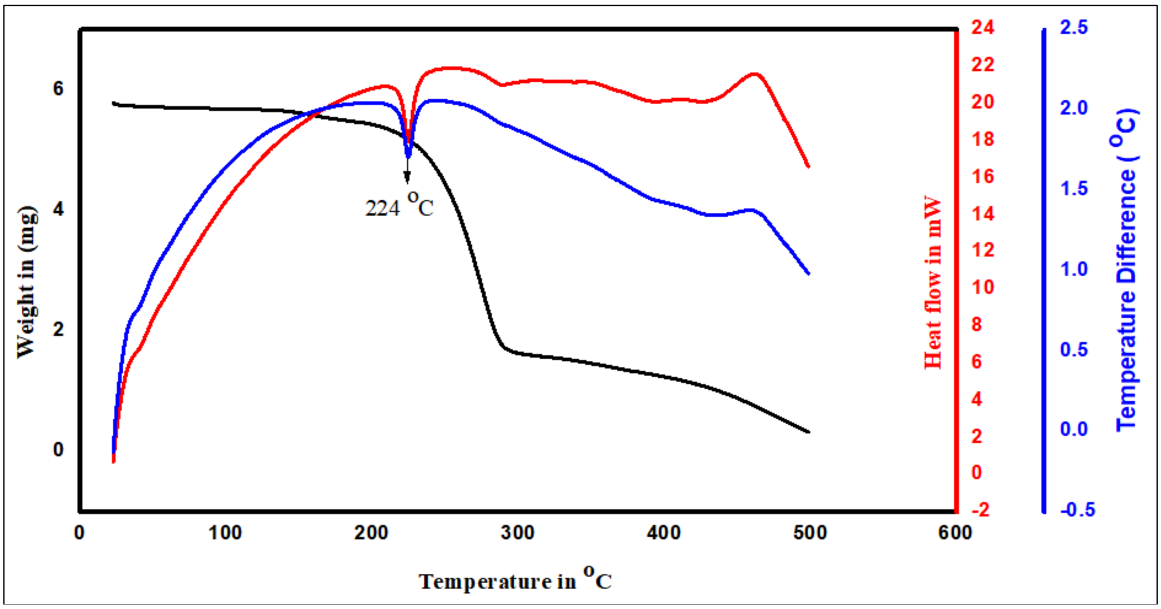

Fig. 2. *The TG/DTA/DSC Curve of 2AF4N crystal.*

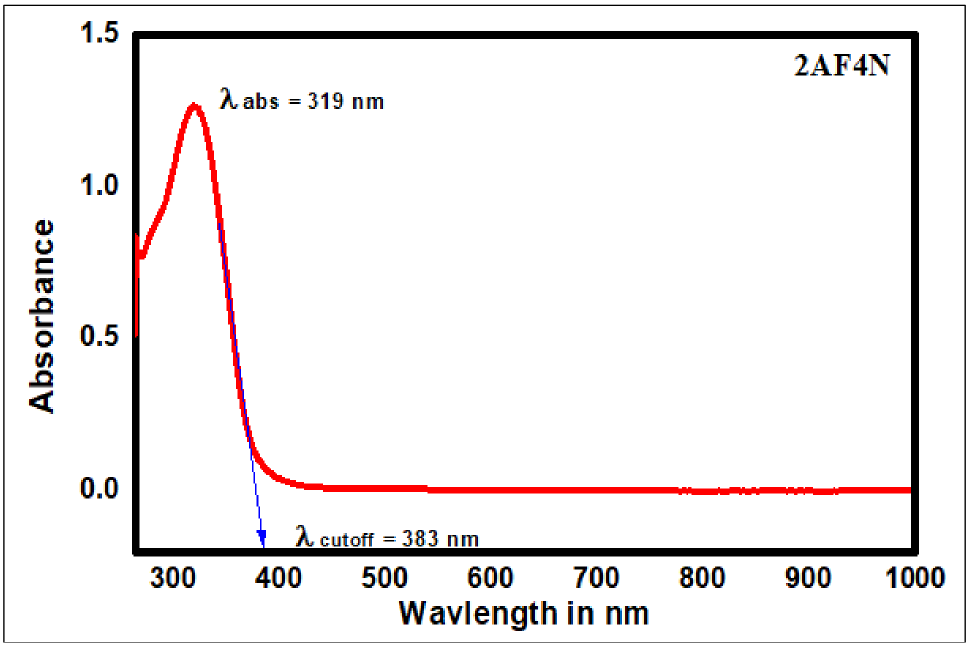

Fig. 3. *The UV-Visible spectra of 2AF4N crystal*

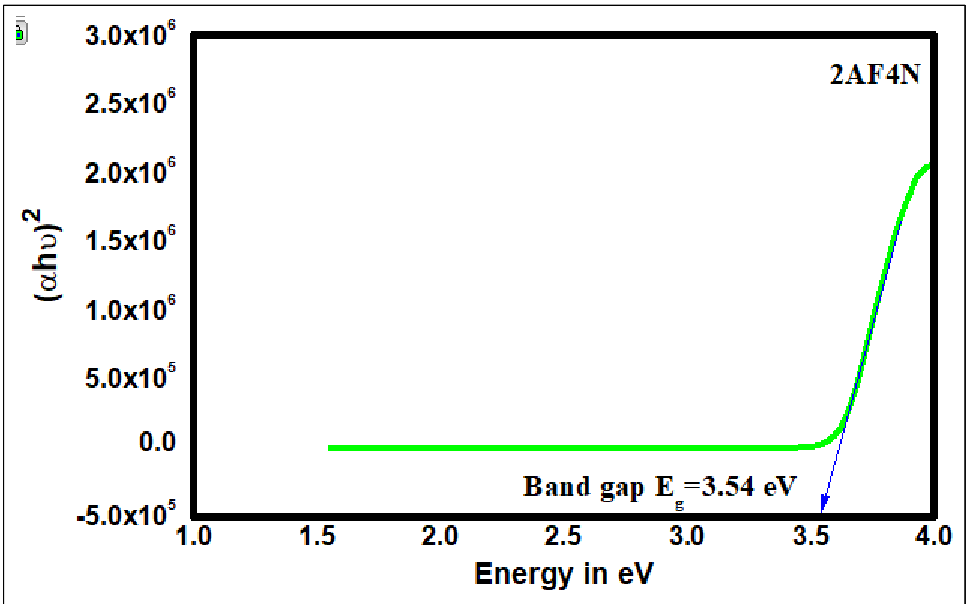

Fig. 4. *Optical band gap of 2AF4N crystal.*

CONCLUSION

A furan based D-π-A type organic single crystals were grown by slow evaporation technique. FTIR studies confirm the functional group activity in the molecule. A thermal study (TG/DTA/DSC) confirms the material stability up to their melting point (224 °C). The noticed optical band gap (3.54 eV) and high transparency range beyond the cut-off (383 nm) in the curve indicates that 2AF4N crystals are suitable in optoelectronic and photonic applications.

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REFERENCES

[1] J. Zyss, Molecular Nonlinear Optics: Materials, Physics and Devices, Academic Press, New York, 1994.

[2] M.D. Aggarwal, W.S. Wang, K. Bhat, B.G. Penn, D.O. Frazeir, in: H.S. Nalwa (Ed.), Handbook of Advanced Electronic and Photonic Materials and Devices, vol. 9, Academic Press, USA, 2001, p. 193.

[3] A. Praveen, A. Jayarama, and S. Weng, "Crucial role of molecular planarity on the second order nonlinear optical property of pyridine based chalcone single crystals," *J. Mol. Struct.*, vol. 1088, pp. 85–94, 2015.

[4] A.J. Kiran, H.C. Kim, K. Kim, F. Rotermund, H.J. Ravindra, S.M. Dharmaprakash, H. Lim, Appl. Phys. Lett. 92 (2008) 113307

[5] A. Ekbote, P. S. Patil, S. R. Maidur, and T. Shyang, "Dyes and Pigments Structural, third- order optical nonlinearities and figures of merit of under CW regime : New chalcone derivatives for optical limiting applications," *Dye. Pigment.*, vol. 139, pp. 720–729, 2017.

[6] K. Naseema, Vijayalakshmi Rao, K.V. Sujith, Balakrishna Kalluraya, Curr. Appl. Phys. 10 (2010) 1236–1241.

[7] A. Ekbote, P. S. Patil, S. R. Maidur, T. S. Chia, and C. K. Quah, "Structure and nonlinear optical properties of (E)-1-(4-aminophenyl)-3-(3-chlorophenyl) prop-2-en-1-one: A promising new D-π-A-π-D type chalcone derivative crystal for nonlinear optical devices," *J. Mol. Struct.*, vol. 1129, pp. 239–247, 2017.

[8] S. Raghavendra, C.S. Chidankumar, A. Jayarama, S. M. Dharmaprakash, Mater. Chem. Phys, 149-150 (2015) 487-494.

[9] P. J. Tejkiran, M. S. Brahma Teja, P. Sai Siva Kumar, Pranitha Sankar, Reji Philip, S. Naveen, N. K. Lokanath, G. Nageswara Rao, J. Photochem. Photobiol. A: Chemi, 324 (2016) 33–39.

[10] S. Satheeshchandra, D. Haleshappa, S. Rohith, A. Jayarama, and N. Shetty, "Novel benzofuran based chalcone material for potential nonlinear optical application," *Phys. B Condens. Matter*, vol. 560, no. January, pp. 191–196, 2019.

[11] H. Davanagere, J. A, P. S. G. Patil, S. R. Maidur, C. K. Quah, and H. C. Kwong, "The structural and third-order nonlinear optical studies of a novel nitro group-substituted chalcone derivative for nonlinear optical applications," *Appl. Phys. A*, vol. 125, no. 5, p. 309, 2019.

[12] S. Anandan, S. Manoharan, N. K. S. Narendran, T. C. S. Girisun, and A. M. Asiri, "Donor- acceptor substituted thiophene dyes for enhanced nonlinear optical limiting," *Opt. Mater. (Amst).*, vol. 85, no. June, pp. 18–25, 2018.

[13] H. A. Khamees, M. Jyothi, S. A. Khanum, and M. Madegowda, "Synthesis, crystal structure, spectroscopic characterization, docking simulation and density functional studies of 1-(3,4-dimethoxyphenyl) -3-(4-flurophenyl)-propan-1-one," *J. Mol. Struct.*, vol. 1161, pp. 199–217, 2018.

[14] D. Haleshappa, A. Jayarama, R. Bairy, S. Acharya, and P. S. Patil, "Second and third order nonlinear optical studies of a novel thiophene substituted chalcone derivative," *Phys. B Condens. Matter*, vol. 555, no. September 2018, pp. 125–132, 2019.

[15] N. Sudharsana, B. Keerthana, R. Nagalakshmi, V. Krishnakumar, L. Guru Prasad, Mater. Chem. Phys. 134 (2012) 736–746.

[16] J. Tauc, R. Grigorovici, A. Vance, Optical properties and electronic structure of amorphous germanium, Phys. Status Solidi B 15 (1966) 627–637.

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