International Journal of ChemTech Research
CODEN(USA): IJCRGG ISSN : 0974-4290
Vol.5, No.6, pp 3051-3058, Oct-Dec 2013

Spectroscopic Studies and other Novel Studies of 4 Bromo 4[l] Chloro Benzylidene Aniline (BCBA) Crystal– A Non Linear Optical Material

K.Senthilkannan[1]*, S.Gunasekaran[1]

[1]Spectrophysics laboratory, Pachaiyappa's College Chennai 600030, TN, India.

***CorresAuthor: mscgoldmedalist@yahoo.in,**
Phone: +91 90424 03418,

Abstract: The organic NLO material of 4-bromo-4[l] chloro benzylidene aniline (BCBA) was synthesized and single crystal of BCBA was grown up from acetone solution by solution growth method. Synthesized compound of BCBA was subjected to FTIR and spectral analysis. The optical transmission of BCBA was determined by UV–vis–NIR spectrum and its fluorescence spectrum was also recorded. SEM, EDAX and TGA, DTA were also studied, analysed and recorded.
Key words: Spectroscopic Studies, 4 Bromo 4[l] Chloro Benzylidene Aniline (BCBA) Crystal, Non Linear Optical Material, Novel Studies.

Introduction

In modern years, organic materials with aromatic rings having elevated NLO coefficient, elevated laser damage threshold, little mobility and large band gap find extensive applications (1–9). Some of the published benzylidene aniline derivatives are 4-nitro-4[l] methyl benzylidene aniline (NMBA) (10) and 4-nitro-4[l] methoxy benzylidene aniline (NMOBA) (11), crystallize in non centro symmetric structure and exhibit second order NLO properties. The 4-chloro-4[l] dimethylamino-benzylidene aniline (CDMABA) crystallizes in centro symmetric structure and its third order NLO considerations were reported. (12). The crystal structure of one of the derivatives of benzylidene aniline, 4-bromo-4[l] chloro benzylidene aniline (BCBA) was reported earlier(13-21). The grown BCBA crystal was characterized by the X-ray powder diffraction (XRPD), and Fourier transform infrared (FTIR) spectral analyses and their SEM, EDAX and TGA, DTA were also studied and recorded, reported.

Synthesis

BCBA was synthesized by the reaction of p bromoaniline (p-BA) and p-chlorobenzaldehyde (p-CB) in stoichiometric ratio. The reaction mixture was refluxed in ethanol about half a day nearly 12h at 90° C and then cooled, which capitulated a pale yellow product of BCBA specimen. The reaction mechanism is in Figure 1. The material was purified from ethanol by recrystallization process. Single crystals of BCBA were grown from acetone solution by the solvent evaporation. In the solvent evaporation, transparent crystal of dimension 6mm×2mm×2mm was obtained in a growth period of 12-14 days. The XRD crystal pattern with parameters for BCBA is given in Table1 with earlier reference workings on BCBA.

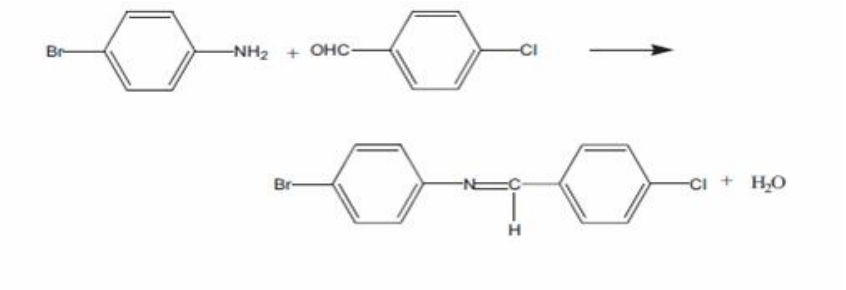


Fig.1. Reaction mecahanism of BCBA

Table.1.Crystal parameters of BCBA comparison with Earlier workings

Parameters	Present Work	Earlier Work II REF(29)	Earlier Work I REF(12)
a(Å)	24.990	24.992	24.880
b(Å)	6.285	6.282	6.379
c(Å)	7.335	7.322	7.436
Angle	α = β = γ = 90˚	α = β = γ = 90˚	α = β = γ = 90˚
Volume($Å^3$)	1152	1149	1180
Crystal System	Orthorhombic	Orthorhombic	Orthorhombic
Space Group	Pccn	Pccn	Pccn

Fourier Transforms Infrared (FTIR) Spectral Analysis

Infrared spectroscopy is efficiently employed to conclude the molecular structure and the detection of the functional groups in the compounds. The FTIR spectrum of BCBA is in the range 500–4000 cm^{-1} (Fig.2). Benzylidene anilines display their C=N stretching vibration at about 1600 cm^{-1} (22-26). Thus the band obtained at approximately 1593 cm^{-1} confirms the formation of group (C=N) as a result of the condensation reaction between aldehydes and amines. Substituted benzenes show C–H deformation vibration in the region 800–840 cm^{-1} and in this work the C–H deformation vibration appears at approximately 825 cm^{-1}. The band at approximately 713 cm^{-1} is due to chlorinated aromatic C–Cl stretching and the absorption band at approximately 531 cm^{-1} is assigned to aromatic C–Br stretching. Thus the FTIR spectral analysis confirms the formation of the BCBA. The experimental values of FTIR are tabulated in Table 2.

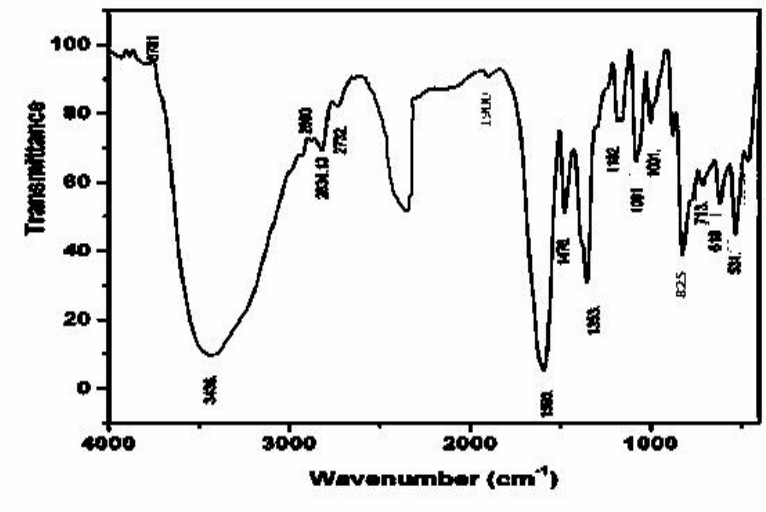


Fig.2. FTIR Spectrum of BCBA

Table 2. FTIR Assignment for BCBA

Wave number in cm^{-1}	Vibrational modes
1593 (Strong)	ν (C=N) Stretching
825 (Strong)	δ (C-H) Bending / deformation
713 (Medium)	ν (C-Cl) Stretching
531 (Strong)	ν (C-Br) Stretching

Powder X-Ray Diffraction

Powder X-ray diffraction patterns were recorded using powder X-ray diffractometer, finely crushed powder of BCBA crystal was scanned in the values ranging from 20◦ to 50◦ and the intensity value between 0 to 2000 and the corresponding peaks were indexed and are shown in Fig.3.

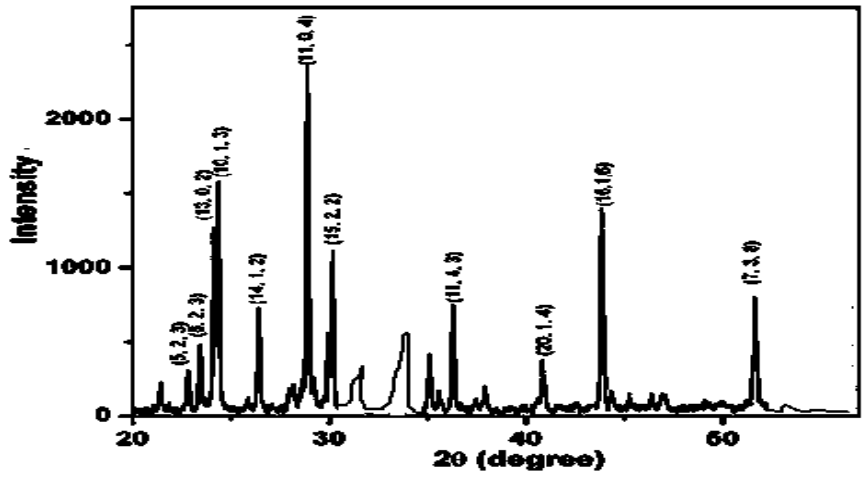


Fig.3. Powder XRD pattern of BCBA

Fluorescence Studies

Fluorescence commonly found in compounds which contains aromatic functional groups through low energy $\pi \rightarrow \pi^*$ transition stages or levels. Fluorescence occurs when an orbital electron of a molecule, atom relaxes to its ground state by emitting a photon of light to a higher state by some type of energy. Compounds containing aliphatic and alicyclic carbonyl structures or toweringly conjugated double bond configurations which exhibit fluorescence, but the number of these are small compared with the number in the aromatic systems (27). Fluorescence finds broad applications in the many research fields for analyzing organic compounds (28). The spectrum given in Fig. 4 shows a peak at ~ 410 nm and indicates that a BCBA crystal has a violet fluorescence emission spectrum.

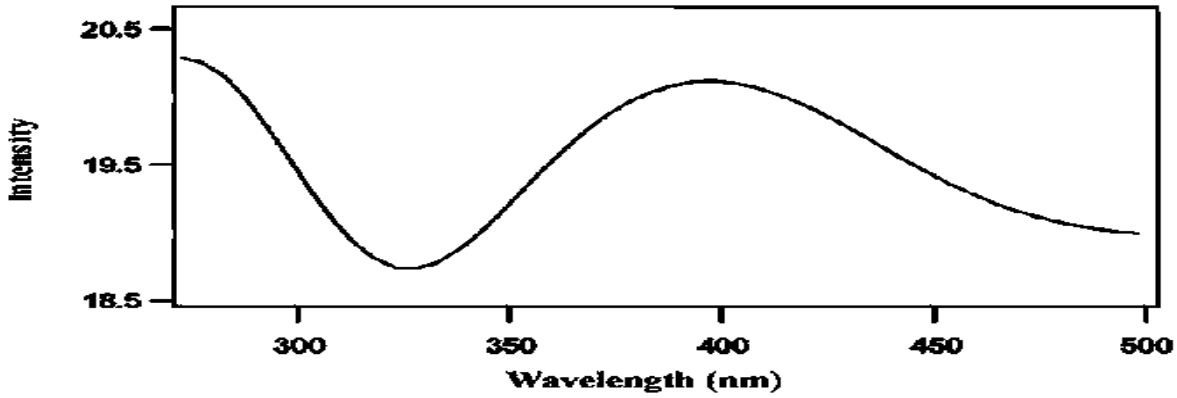


Fig.4. Fluorescence spectrum of BCBA

UV-Vis Spectra

The optical transmission spectrum gives valuable information about the structure of the molecules because the absorption of UV and visible light involves promotion of orbital electrons from the ground state to an elevated energy state (26). Transmittance spectrum of the BCBA crystal recorded using UV–vis–NIR spectrophotometer and is presented in Fig. 5. Optically clear crystal of thickness about 2 mm was used for this study. The UV cut-off wavelength for the grown crystal is observed at approximately 450 nm.

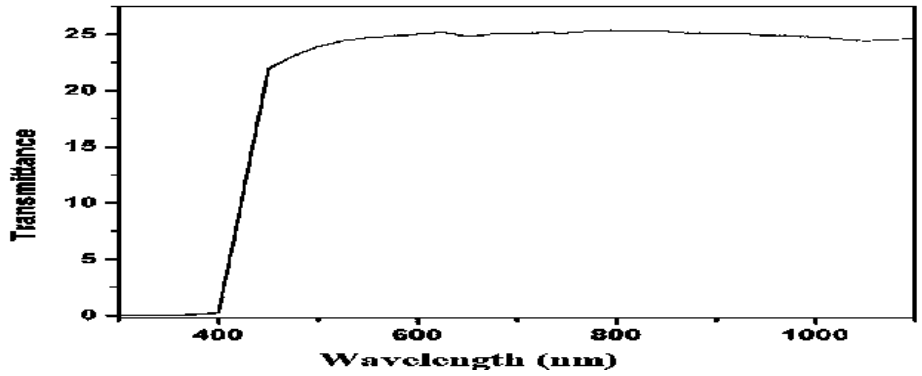


Fig.5.UV Vis Spectrum of BCBA

High-Resolution (HR) SEM

By high-resolution (HR) SEM, it signifies imaging of the specimen with high precision, to represent the surface morphology. In HR SEM a field emission gun and appropriate electron optics that converge the beam in to a narrow (in the order 1 nm of diameter) electron probe with high intensity. A detector that removes any possible signal from backscattered electrons, since their large interaction corrupts image resolution. To study surface morphology of the material SEM is effectually used. Figure 6 a, b, c shows the SEM images of BCBA crystal with the instrument specifications of 1250 SEI with 20kV potential with 1500, 3500 and 7000 resolutions and of 10µm, 5µm, 2µm dimensions of thickness. Thus from the SEM study it clearly portrays that the monoclinic crystal has no major defects and free from deforms and flaws and has no major dislocations. From SEM images it is clear that the grown title material has no major defects on the surface and substantiates the growth of good quality single materials.

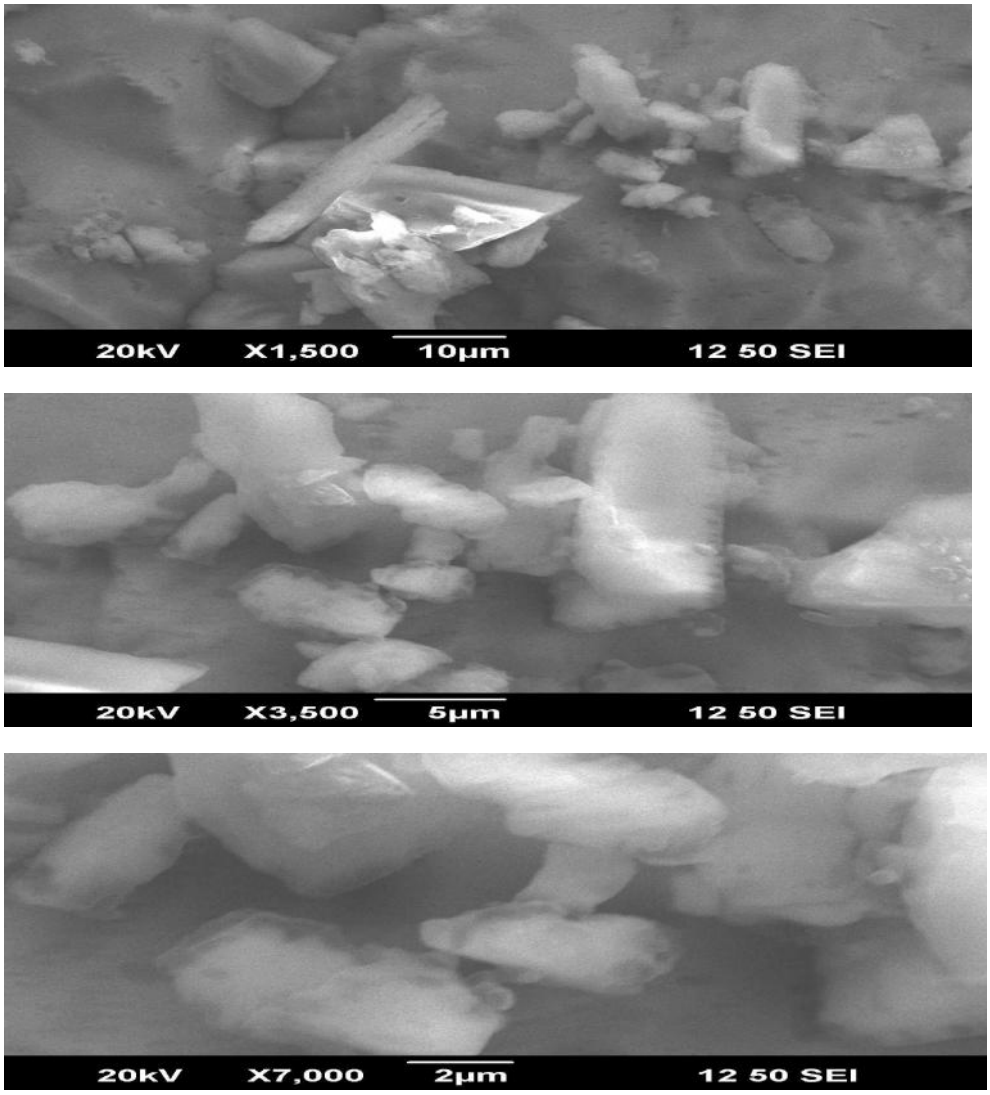


Fig.6.a,6b,6c. SEM images at 3 different resolutions for BCBA crystal

EDAX – Energy Dispersive X-Ray Analysis

The high energy electron beam ejects electrons from inner-shell atomic orbitals in the sample. The resulting vacancies are filled by electrons from higher energy shells; electron energies lost during these transitions are emitted as X-rays. Therefore, measuring the X-ray spectrum allows identification of the sample composition. The detected X-rays normally get from a large, sub-surface interaction volume that can measure on the order of a µ m in size. This frequently limits the spatial resolution of EDX in the SEM. It is one of the variants of X-ray fluorescence spectroscopy which relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing X-rays emitted by the matter in response to being hit with charged particles. Fig 7 shows the EDAX graph of BCBA which is Counts Vs Energy in keV. It gives the qualitative and quantitative information of the elements present in the specimen.

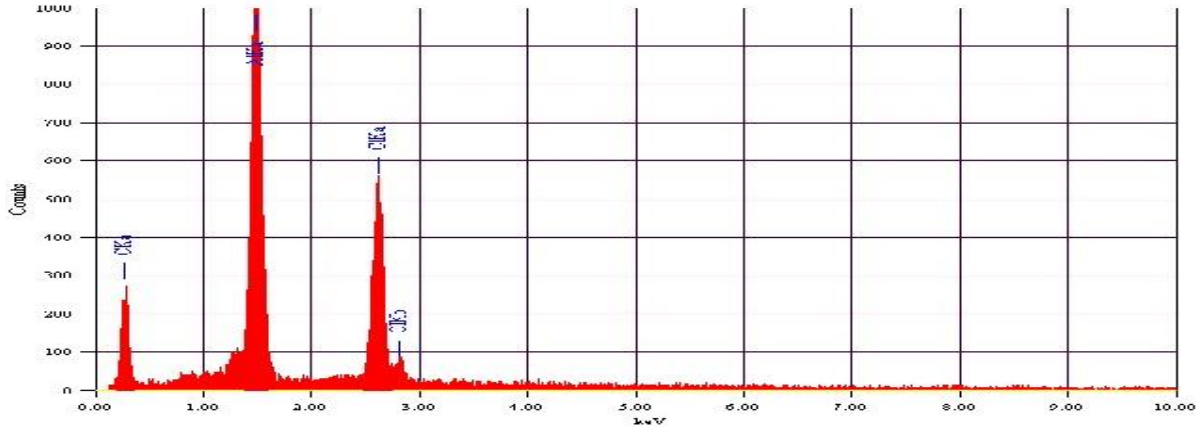
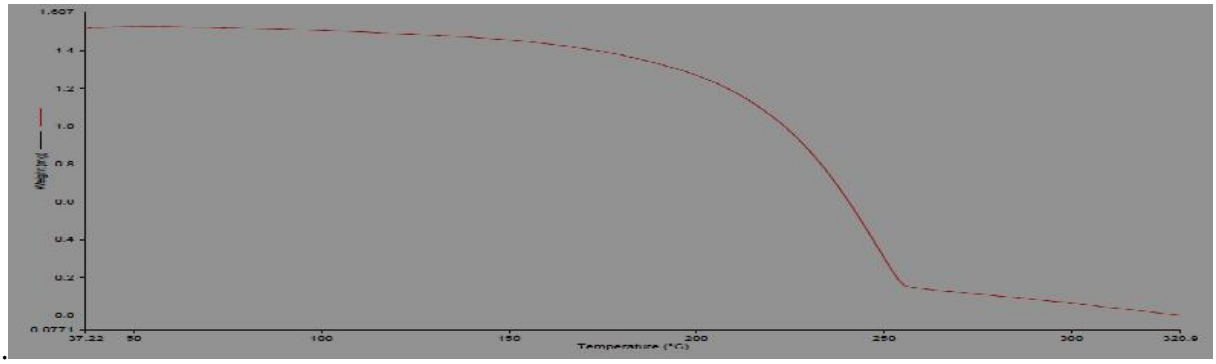


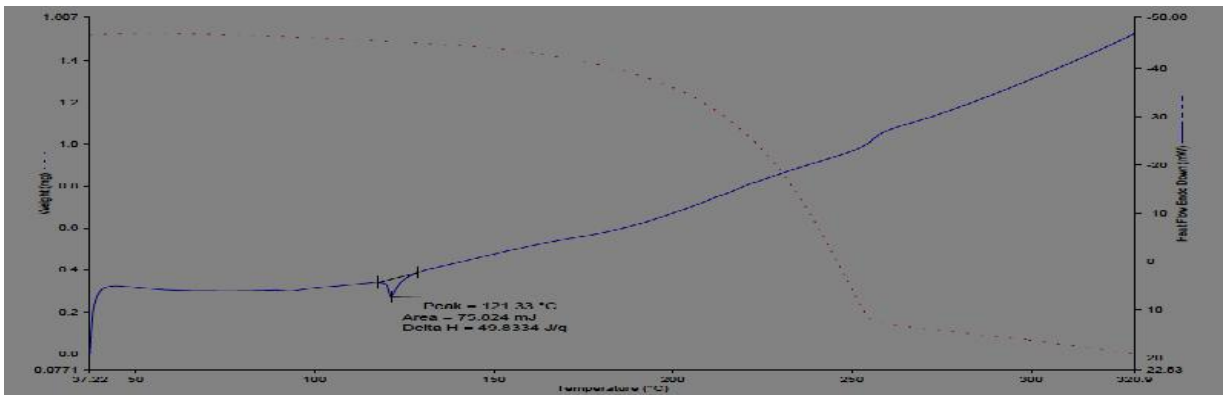
Fig.7.EDAX graph for BCBA

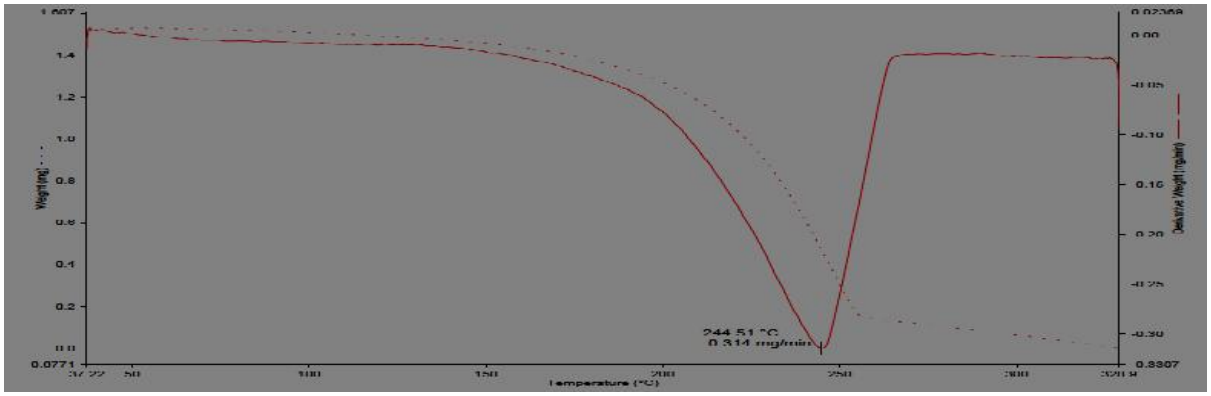
Thermo Gravimetric Analysis (TGA) & Differential Thermal Analysis (DTA)

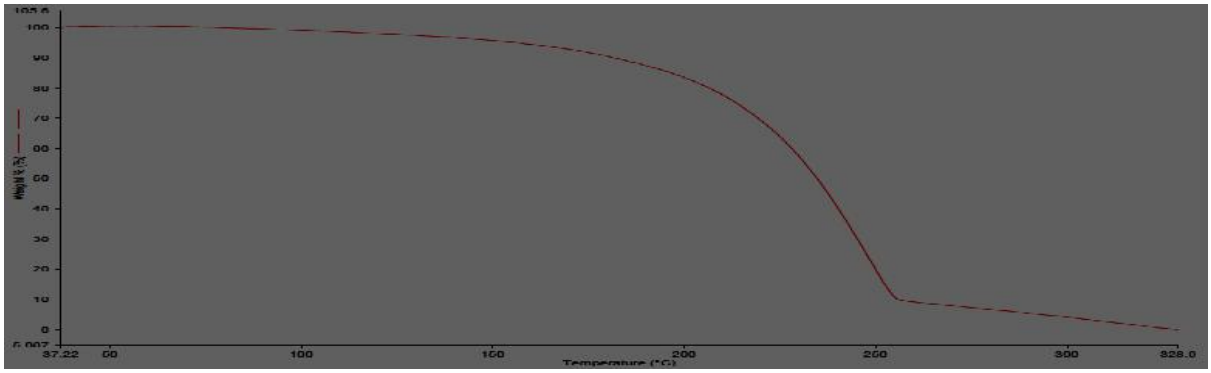
Thermo gravimetric Analysis (TGA) when complemented with differential thermal analysis (DTA) gives valuable information about decomposition patterns of materials and weight loss can be obtained. Also phase transitions can be obtained. The temperature range is from room temperature to nearly 330^{o}C with a bend around 260 ^{o}C in the weight Vs Temperature graph in Fig.8a, b, c, d. In the second graph as in shown, the weight Vs Temperature with heat flow in mW along parallel Y axis with an area value of 75mJ and change in energy value as 49.8334 J/g and the peak is at 121.33 ^{o}C. From the thermogram the melting point is identified as 121.33 ^{o}C. In the third graph as shown, it specifies weight Vs Temperature with derivative weight along parallel Y axis with a value 244.51^{o}C with -0.314 mg/min and the fourth graph is Weight % Vs Temperature it shows the stepping down peak around 260^{o}C. This shows that the BCBA crystal is stable up to 170^{o}C with which no phase transition observed in this province.

Fig.8. TGA and DTA for BCBA









Conclusions

The organic NLO material 4bromo-4[l]chloro benzylidene aniline synthesized was confirmed by FTIR spectral analyses. Acetone was identified as the suitable solvent to grow visible crystal. Single crystal X-ray diffraction study confirmed that the grown BCBA crystal belongs to the orthorhombic system with space group Pccn. Optical transparency of the crystal is in the region of 450–1000 nm. The BCBA crystal reveals violet fluorescence emission. The SEM, EDAX and TGA & DTA are also studied and we got crystal morphology and melting point details of the BCBA crystal.

Acknowledgements

The Authors acknowledge their thanks to SAIF-IITM chennai for characterisation / studies and Dr. K. Ramamurthy - Bharathidasan University, Tiruchirappalli 620 024, India for his valuable suggestions and guidance and Madam Ka.Seethalakshmi Phoenix Institute for her support.

References

1. J.P. Farges, Organic Conductors, Marcel Dekker, New York, 1994.
2. T. Ishiguro, K. Yamaji, Organic Superconductors, Springer, Berlin, 1990.
3. Ch. Bosshard, K. Shutter, Ph. Pretre, J. Hulliger, M. Florsheimer, P. Kaatz, P. Gunter, Organic NLOM, Gordon and Breach, London, 1995.
4. S.X. Dou, D. Josse, J. Zyss, J. Opt. Soc. Am. B 10 (1993) 1708–1715.
5. A.M. Petrosyan, J. Crystallization Phys. Chem. 1 (2010) 33–56.
6. J. Badan, R. Hierle, A. Perigaud, J. Zuss, NLO properties of organic molecules and polymeric materials, in: D.J. Williams (Ed.), American Chemical Society Symposium Series, vol. 233, American Chemical Society, Washington, DC, 1993.

7. P.N. Prasad, D.J. Williams, Introduction to Nonlinear Optical Effects in Organic Molecules and Polymers, Wiley, New York, 1991.
8. D. Balasubramanian, R. Sankar, V. Siva Sankar, P. Murugakoopthan, P. Arulmozhichelvan,R. Jeyavel, Mater. Chem. Phys. 107 (2008) 57–60.
9. S. Leela, K. Ramamurthi, H.S. Evans, G. Vasuki, Acta Crystallogr. E 63 (2007) 4805.
10. K. Srinivasan, R. Biravaganesh, R. Gandhimathi, P. Ramasamy, J. Cryst. Growth 236 (2002) 381–392.
11. A.N. Azariah, A.S.H. Hameed, T. Thennappan, M. Noel, G. Ravi, Mater. Chem. Phys. 88 (2002) 90–96.
12. S. Leela, K. Ramamurthi, G. Bhagavannarayana, Spectrochim. Acta 74A (2009) 78–83.
13. I. Bar, J. Bernstein, Tetrahedron 43 (1987) 1299–1305.
14. X. Zhao, Y. Si, D. Xue, J. Crystallization Phys. Chem. 1 (2010) 57–73.
15. X. Yan, D. Xu, D. Xue, Acta Mater. 55 (2007) 5747–5757.
16. D. Xu, D. Xue, J. Cryst. Growth 286 (2006) 108–113.
17. D. Xu, D. Xue, J. Cryst. Growth 310 (2008) 1385–1390.
18. X. Ren, D. Xu, D. Xue, J. Cryst. Growth 310 (2008) 2005–2009.
19. D. Xu, D. Xue, Physica B 370 (2005) 84–89.
20. Y.R. Sharma, Elementary Organic Spectroscopy, S. Chand, New Delhi, 2000.
21. P. Clerc, S. Simon, Tables of Structure Determination of Organic Compounds, second ed., Springer-Verlag, Berlin, Heiderberg, New York, 1989.
22. C.J. Pouchert, Aldrich Library of FTIR Spectra, third ed., Aldrich Chemical Co. Inc., Milwaukee, 1984.
23. (23)Stoe&Cie, X-Area VI. 52, X-RED32 VI. 48&X-SHAPE Software, Stoe&Cie GmbH, Darmstadt, Germany, 2009.
24. G.M. Sheldrick, Acta Cryst. A64 (2008) 112–122.
25. A.L. Spek, Acta Cryst. D65 (2009) 148–155.
26. S. Dinakaran, Sunil Verma, C. Justin Raj, J. Mary Linet, S. Krishnan, S. Jerome Das, Cryst. Growth Des. 9 (2009) 151–155.
27. D.A. Skoog, Principles of Instrumental Analysis, first ed., Holt, Rinehart and Winston,NewYork, 1971.
28. H.H. Willard, L.L. Merritt Jr., J.A. Dean, F.A. Settle Jr., Instrumental Methods of Analysis, sixth ed., Wadsworth Publishing Company, USA, 1986.
29. A. Subashini, R. Kumaravel, S. Leela, Helen Stoeckli Evans, D. Sastikumar, K. Ramamurthi
Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 78 (2011) 935–941.

*****