Journal of Thermal Analysis and Calorimetry, Vol. 94 (2008) 1, 59–62

GROWTH AND CHARACTERIZATION STUDIES OF 2-BROMO-4'-CHLOROACETOPHENONE (BCAP) CRYSTALS

G. Madhurambal[1], *P. Ramasamy*[2], *P. Anbusrinivasan*[3], *G. Vasudevan*[3], *S. Kavitha*[3] *and S. C. Mojumdar*[4,5*]

[1]ADM College for Women, Nagapattinam, Tamilnadu, India
[2]Crystal Growth Center, Anna University, Chennai, Tamilnadu, India
[3]AVC College, Mayiladuthurai, Tamilnadu, India
[4]Department of Chemical Engineering and Applied Chemistry, University of Toronto, 200 College St., Toronto, ON, M5S 3E5, Canada
[5]University of New Brunswick, Saint John, NB, E2L 4L5, Canada

2-bromo-4-chloroacetophenone (BCAP) crystals were grown from carbon tetrachloride as solvent using slow evaporation technique at room temperature. Transparent, good quality BCAP crystals were successfully grown. Solubility studies were made using this solvent at various temperatures. The various functional groups present in the grown crystal have been identified using FTIR spectra. The grown crystals were subjected to ^{1}H NMR studies and thermal studies in order to confirm the structure and purity of the grown crystals respectively. The transparency of the crystal was tested using UV-visible spectral analysis. The unit cell dimensions of grown crystal were determined for the first time. Solubility and metastable zone width studies of BCAP in CCl_4 have been carried at various temperatures.

Keywords: *2-bromo-4'-chloroacetophenone, characterization studies, DTA, solution technique, TG, unit cell dimensions*

Introduction

Non-linear optics (NLO) has wide applications in the field of telecommunication and optical information storage devices. The organic NLO materials play an important role in second harmonic generation (SHG), frequency mixing, electro-optic modulation, optical parametric oscillation, optical bi-stability, etc. [1]. Organic crystals have parameters superior to widely used crystals like KDP [2–4]. Many authors investigated various organic and organometallic compounds due to their very important roles in chemical, biological, electrical and environmental sciences and also examined their various properties [5–42]. Chenthamarai *et al.* [43] reported the growth of good quality 4-hydroxyacetophenone and nitro doped 4-hydroxyacetophenone crystals from the saturated methanol solution by slow cooling method. The single crystals of organic non-linear optical material, 2-amino-5-chloro benzophenone were grown by the slow evaporation solution growth technique using acetone as solvent [44]. Investigation on the solution growth and characterization of indole-3-carbaldehyde [45], methyl-4-hydroxybenzoate [46] and benzaldehyde semicarbazone [47] were reported recently. But there is no report available in the literature about the solution growth of BCAP and its characterization studies. BCAP is one of the new organic nonlinear crystal having good SHG efficiency. In this paper, the solution growth of BCAP, its characterization studies and determination of unit cell dimensions is reported for the first time. In this present study, the solubility of BCAP has been determined in CCl_4 solvent. After solubility determination, the crystals were grown from CCl_4 using slow evaporation technique at room temperature. The crystals were carefully harvested and subjected to various characterization studies viz. UV, FTIR, ^{1}H NMR spectra and TG-DTA. The results are suitably interpreted.

Experimental

BCAP and CCl_4 solvent were analytic grade (E-Merck) samples. The analytic sample of BCAP was purified by repeated recrystallization. It was then taken for crystal growth. Transparent crystals were obtained from the mother solution within a day and the powder of BCAP is used as solute. The solubility study has been done for CCl_4 in different temperatures.

The FTIR spectrum was recorded in the range of 400–4000 cm^{-1} for BCAP sample on an AVATAR330 FTIR spectrophotometer using KBr pellet technique.

* Author for correspondence: scmojumdar@hotmail.com

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

The UV-Visible spectrum of solution grown BCAP was recorded in CARY 5E UV-VIS-NIR spectrophotometer between 400–1200 nm.

The ^{1}H NMR spectrum of solution grown BCAP was recorded using JEOL GSX400 NMR spectrometer at 400 MHz with a magnectic field of 9.3 Tesla, using $CDCl_3$ as solvent.

The solution grown BCAP was subjected to single crystal X-ray diffraction analysis using ENRAF (BRUKER0 NONIUS CAD4) single crystal X-ray diffractometer.

The BCAP was subjected to thermogravimetric analysis (TG) and derivative thermogravimetric analysis (DTG) using Netzsch STA 409 simultaneous thermal analyses using alumina crucible in nitrogen atmosphere in the temperature range of 28 to 1200°C.

Results and discussion

The solubility of BCAP in CCl_4 is shown in Fig. 1. Metastable zone width is an essential parameter for the growth of good crystals from solution, since it is the direct measure of the stability of the solution in its supersaturated region. The metastable zone width of BCAP in CCl_4 is shown in Fig. 1.

FTIR studies

The solution grown BCAP was subjected to FTIR spectral studies and the FTIR spectrum is shown in Fig. 2. In the spectrum stretching is observed at 3037 cm^{-1}.

The aliphatic C–H bending at 757 cm^{-1} and C–H deformation at 784 cm^{-1} is also observed. The skeletal vibrations of the aromatic ring are observed at 1618, 1589, 1569, 1485 and 1401 cm^{-1}. The carbonyl C=O is observed at 1615 cm^{-1}. The peak at 757 cm^{-1} shows the presence of C–Cl stretching. The C=C–H stretching at 811 and 958 cm^{-1}. In the aromatic ring C=C stretching is found at 1485 to 1559 cm^{-1}. The para substitution is clearly evident by the peaks at 958 and 1115 cm^{-1}.

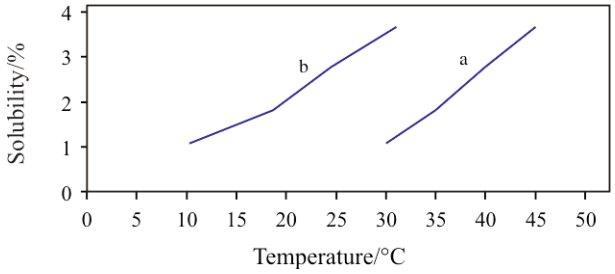


Fig. 1 a – Solubility and b – metastable zone width of BCAP in CCl_4

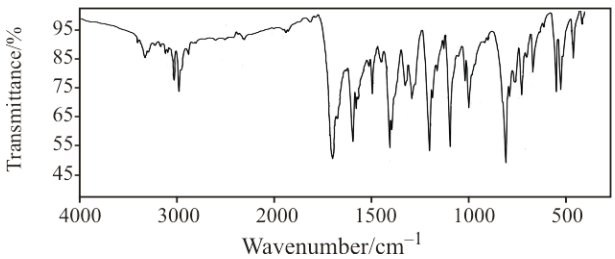


Fig. 2 FTIR spectrum of solution grown of BCAP

UV-Vis analysis

The UV-Visible spectrum is due to the electronic transitions of the molecule. This is characteristic of a compound. The solution grown BCAP was subjected to UV-Visible spectral studies to determine its transparency, which is an important requirement for NLO applications. The absorbance spectrum of BCAP is shown in Fig. 3. The characteristic absorption is found between 300–400 nm which is assigned to aromatic ring. The UV-Visible absorbance spectrum of solution grown BCAP clearly shows that it is completely transparent with about 78% transmission from 400–800 nm and 82% transmission from 800–1200 nm. So it is conveniently used for modulation purposes.

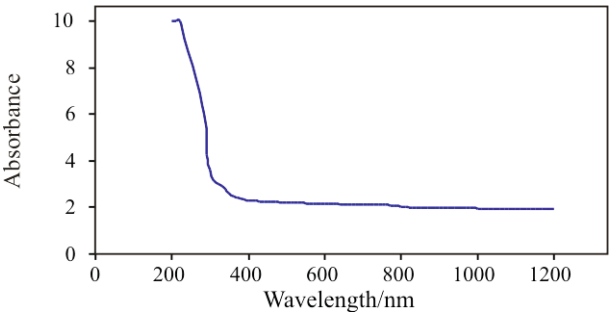
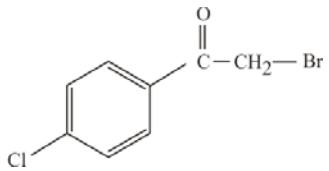


Fig. 3 UV-Visible spectrum of solution grown of BCAP

^{1}H NMR studies

^{1}H NMR spectroscopy is used to determine the molecular structure based on the chemical environment of the magnetic nuclei like ^{1}H, ^{13}C and ^{31}P even at low concentrations. The structure of BCAP is as follows.



Three different kinds of protons a, b and c are present in it which is clearly evident from NMR spectral analysis. The ^{1}H NMR spectrum of solution grown BCAP is shown in Fig. 4. In the spectrum two doublets are present at δ=8.0 and 7.5 which are assigned to protons of the type 'a' and 'b'. The singlet at δ=4.4 is assigned to –CH_2 protons of the type 'c'.

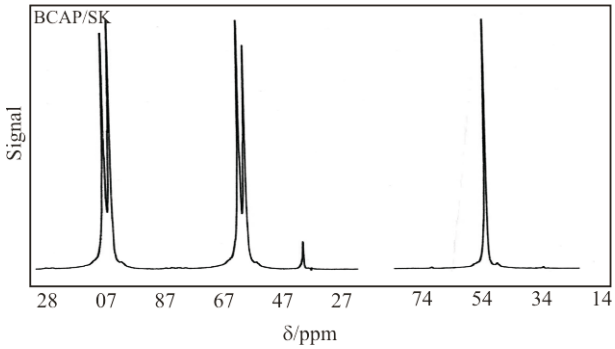


Fig. 4 ^{1}H NMR spectrum of solution grown of BCAP

X-ray diffraction studies

The single crystal XRD studies reveals that the BCAP belongs to orthorhombic crystals and having unit cell dimensions a=4.1336 Å, b=9.558 Å, c=21.6142 Å and $\alpha=\beta=\gamma=90°$. The volume of unit cell is about 853.76 Å^3.

Thermal studies

The TG and DTG curves of BCAP are given in Fig. 5. The TG curve exhibits the two main mass loss steps between rT–275 and 275–575°C, accompanied by 99.85% total mass loss corresponding to the decomposition of BCAP. The DTG curve showed two corresponding DTG peaks at 245.5 and 535°C.

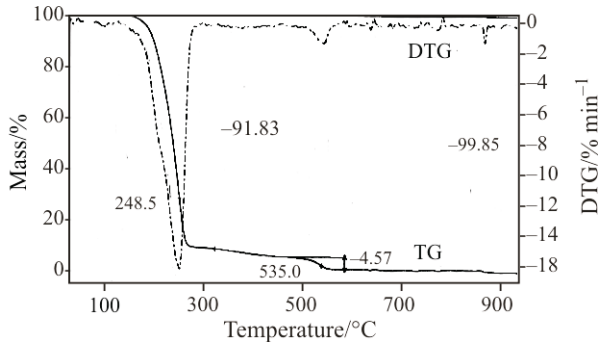


Fig. 5 TG-DTG curves of solution grown of BCAP

Conclusions

A new NLO material 2-bromo-4'-chloroacetophenone (BCAP) was grown from solvent CCl_4 using slow evaporation technique at room temperature. Solubility of BCAP at different temperatures was determined. The solution grown BCAP was also subjected to various characterization studies to check its purity and determine its applications. UV spectral study shows the transparency of the BCAP. FTIR and ^{1}H-NMR spectral studies support the structure and purity of BCAP. XRD patterns shows different planes and expected structure of solution grown BCAP.

The SHG efficiency of BCAP was also determined and compared with the SHG efficiency of KDP crystals, which is well known semi-organic NLO crystals. BCAP is found to be 0.83 times SHG efficiency compared to KDP crystals.

References

1 J. Badan, R. Hierle, A. Perigaud and J. Zyss, American Chemical Society Symposium Series, Vol. 233, D. J. Williams, Ed, American Chemical Society, Washington D. C. 1993.
2 D. Chemla and J. Zyss, Nonlinear Optical Properties of Organic Materials and Crystals, Academic Press, New York 1987.
3 T. Sasaki, A. K. Fujioka, T. Yamanka, S. Nakai and C. Yamanaka, NLO Organic Semiconductors, T. Kobayashi, Ed., Springer Proceedings in Physics, Vol. 36, Springer, Berlin 1989.
4 L. I. Zhendeng, W. U. Biachang and S. U. Genbo, J. Cryst. Growth, 178 (1997) 539.
5 R. N. Patel and K. B. Pandeya, J. Inorg. Biochem., 72 (1998) 109.
6 S. C. Mojumdar, M. Sain, R. Prasad, L. Sun and J. E. S. Venart, J. Therm. Anal. Cal., 90 (2007) 653.
7 H. S. Rathore, G. Varshney, S. C. Mojumdar and M. T. Saleh, J. Therm. Anal. Cal., 90 (2007) 681.
8 S. C. Mojumdar, I. Capek, P. Capek, L. Fialová and D. Berek, Res. J. Chem. Environ., 11 (2007) 5.
9 D. Czakis-Sulikowska, A. Czylkowska and A. Malinowska, J. Therm. Anal. Cal., 67 (2002) 667.
10 S. C. Mojumdar, K. Lebrušková and D. Valigura, Chem. Papers, 57 (2003) 245.
11 K. G. Varshney, A. Agrawal and S. C. Mojumdar, J. Therm. Anal. Cal., 90 (2007) 721.
12 C. Elliot, Z. Ye, S. C. Mojumdar and M. T. Saleh, J. Therm. Anal. Cal., 90 (2007) 707.
13 M. Enamullah and W. Linert, J. Coord. Chem., 35 (1995) 325.
14 G. Madhurambal, P. Ramasamy, P. A. Srinivasan and S. C. Mojumdar, J. Therm. Anal. Cal., 90 (2007) 673.
15 K. G. Varshney, A. Agrawal and S. C. Mojumdar, J. Therm. Anal. Cal., 90 (2007) 731.
16 S. Meenakshisundaram, S. Parthiban, G. Madhurambal, R. Dhanasekaran and S. C. Mojumdar, J. Therm. Anal. Cal., DOI: 10.1007/s10973-008-9181-1.
17 S. C. Mojumdar, M. Melník and E. Jóna, J. Anal. Appl. Pyrolysis, 53 (2000) 149.
18 G. Madhurambal, P. Ramasamy, P. AnbuSrinivasan, M. Suganthi, G. Vadusevan and S. C. Mojumdar, J. Therm. Anal. Cal., DOI: 10.1007/s10973-008-9186-9.
19 B. Borah and J. L. Wood, Canad. J. Chem., 50 (1976) 2470.
20 S. C. Mojumdar, K. G. Varshney and A. Agrawal, Res. J. Chem. Environ., 10 (2006) 89.
21 H. S. Rathore, K. Ishratullah, C. Varshney, G. Varshney and S. C. Mojumdar, J. Therm. Anal. Cal., DOI: 10.1007/s10973-008-9191-z.

22 A. Ramadevi and K. Srinivasan, Res. J. Chem. Environ., 9 (2005) 54.
23 S. Meenakshisundaram, S. Parthiban, G. Madhurambal and S. C. Mojumdar, J. Therm. Anal. Cal., DOI: 10.1007/s10973-008-9182-0.
24 R. N. Patel and K. B. Pandeya, Synth. React. Inorg. Met.-Org. Chem., 28 (1998) 23.
25 J. S. Skoršepa, K. Györyová and M. Melník, J. Thermal Anal., 44 (1995) 169.
26 D. Ondrušová, E. Jóna and P. Šimon, J. Therm. Anal. Cal., 67 (2002) 147.
27 E. Jona, E. Rudinska, M. Sapietova, M. Pajtasova and D. Ondrusova, Res. J. Chem. Environ., 10 (2006) 31.
28 M. Kubranová, E. Jóna, E. Rudinská, K. Nemčeková, D. Ondrušová and M. Pajtášová, J. Therm. Anal. Cal., 74 (2003) 251.
29 E. Jóna, M. Hvastijová and J. Kohout, J. Thermal Anal., 41 (1994) 161.
30 D. Czakis-Sulikowska and A. Czylkowska, J. Therm. Anal. Cal., 71 (2003) 395.
31 S. C. Mojumdar, M. Melník and E. Jóna, J. Therm. Anal. Cal., 56 (1999) 533.
32 S.C. Mojumdar, L. Martiška, D. Valigura and M. Melník, J. Therm. Anal. Cal., 74 (2003) 905.
33 E. A. Ukraintseva, V. A. Logvinenko, D. V. Soldatov and T. A. Chingina, J. Therm. Anal. Cal., 75 (2004) 337.
34 S. C. Mojumdar, M. Melník and E. Jóna, J. Therm. Anal. Cal., 56 (1999) 541.
35 M. T. Saleh, S. C. Mojumdar and M. Lamoureux, Res. J. Chem. Environ., 10 (2006) 14.
36 S. C. Mojumdar, G. Madhurambal and M. T. Saleh, J. Therm. Anal. Cal., 81 (2005) 205.
37 K. G. Varshney, A. Agrawal and S. C. Mojumdar, J. Therm. Anal. Cal., 81 (2005) 183.
38 E. Jóna, E. Rudinská, M. Sapietová, M. Pajtášová, D. Ondrušová, V. Jorík and S. C. Mojumdar, Res. J. Chem. Environ., 9 (2005) 41.
39 S. C. Mojumdar, J. Miklovic, A. Krutošíková, D. Valigura and J. M. Stewart, J. Therm. Anal. Cal., 81 (2005) 211.
40 S. C. Mojumdar, Res. J. Chem. Environ., 9 (2005) 23.
41 G. Madhurambal, S. C. Mojumdar, S. Hariharan and P. Ramasamy, J. Therm. Anal. Cal., 78 (2004) 125.
42 S. C. Mojumdar, J. Therm. Anal. Cal., 64 (2001) 629.
43 S. Chenthamarai, Cryst. Engineer., 4 (2001) 37.
44 R. RameshBabu, N. Vijayan, M. Gunasekaran, R. Gopalakrishnan and P. Ramasamy, J. Cryst. Growth, 265 (2004) 290.
45 S. H. Hameed, G. Ravi, R. Dhanasekaran and P. Ramasamy, J. Cryst. Growth, 212 (2000) 227.
46 N. Vijayan, R. RameshBabu, M. Gunasekaran, R. Gopalakrishnan and P. Ramasamy, J. Cryst. Growth, 256 (2003) 174.
47 R. RameshBabu, N. Vijayan, R. Gopalakrishnan and P. Ramasamy, J. Cryst. Growth, 240 (2002) 545.

DOI: 10.1007/s10973-008-9188-7