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Growth and Characterization Studies of 2-Bromo-4-chloroacetophenone Crystals

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The crystals of 2-bromo-4-chloroacetophenone (BCAP) 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 were tested using UV-Visible spectral analysis. Solubility and metastable zone width studies of BCAP in CCl_4 have been carried at various temperatures. SHG efficiency of the grown crystals was analyzed by kurtz powder technique.

Key Words: 2-Bromo-4-chloroacetophenone, Solution technique, Characterization studies, Unitcell dimensions, Second harmonic generation efficiency.

INTRODUCTION

NLO (non-linear optics) has wide applications in the field of telecommunication and optical information storage devices. The organic NLO materials play an important role in 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]. Chenthamarai *et al.*[5] reported the growth of good quality 4-hydroxy acetophenone and nitro doped 4-hydroxy acetophenone 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[6]. Recently studies on the solution growth and characterization of indole-3-aldehyde[7], methyl-4-hydroxy benzoate[8], benzaldehyde semicarbazone[9] were reported. The solution growth of anthracene from CCl_4 was also reported[10]. But there was no reports available in the literature about the solution growth of BCAP and its characterization studies.

2-Bromo-4-chloroacetophenone (BCAP) is one of the new organic nonlinear crystal having good second harmonic generation (SHG) efficiency. In this paper, the solution growth of BCAP, its characterization studies and determination of unit cell dimensions is reported. 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, TGA-DTA.

EXPERIMENTAL

2-Bromo-4-chloroacetophenone (BCAP) and CCl_4 solvent were AnalaR grade (E-Merck) samples. The analar 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. Here the powder of BCAP is used as solute. The solubility study has been done for CCl_4 in different temperatures (30-45 ºC). 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.

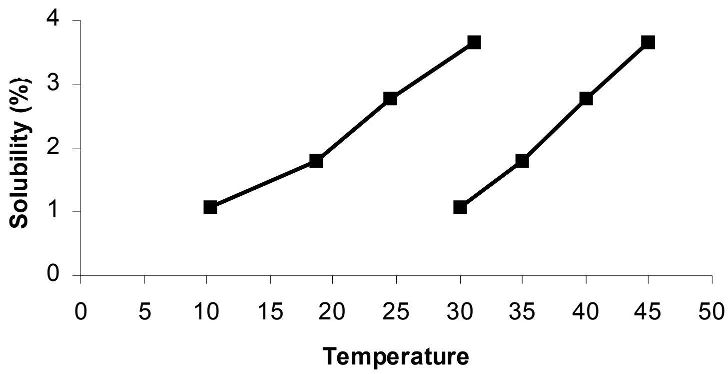


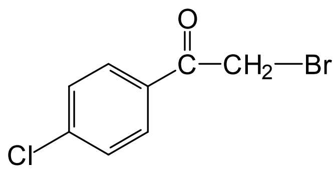
Fig. 1. Solubility and Metastable zonewidth of BCAP in CCl_4

RESULTS AND DISCUSSION

The solution grown BCAP was subjected to FTIR spectral studies. The FTIR spectrum was recorded in the range of 4000-400 cm^{-1} for BCAP sample were performed in AVATAR330 FTIR spectrophotometer using KBr pellet technique. In the spectrum C-H stretching at 1437 cm^{-1} is observed. Aromatic C-H 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}.

The solution grown BCAP was subjected to UV-Visible spectral studies to determine its transparency, which is an important requirement for NLO applications. The UV-Visible spectrum of solution grown BCAP was recorded in CARY 5E UV-Vis-NIR spectrophotometer between 400-1200 nm. The absorbance spectrum of BCAP. In this spectrum, 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.

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



Three different kinds of protons a, b, c are present in it. It is clearly evident from NMR spectral analysis.The ^{1}H NMR spectrum of solution grown BCAP. In the spectrum two doublets are present at δ8.0 and δ7.5 which are assigned to protons of the type 'a' and 'b'. The singlet at δ4.4 is assigned to $-CH_2$ protons of the type 'c'.

The solution grown BCAP was subjected to single crystal X-ray diffraction analysis using Bruker Nonius CAD4 single crystal X-ray diffractometer. 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 α = 90º, β = 90º, γ = 90º. The volume of unit cell is about 853.76 Å^3.

The BCAP was subjected to thermogravimetric analysis and differential thermal analysis using Netzsch STA 409 simultaneous thermal analyses using alumina crucible in nitrogen atmoshere in the temperature range of 28-1200 ºC.

The thermogram of solution grown BCAP, supports the high purity and high thermal stability of the solution grown BCAP.

Secondary harmonic generation (SGH) efficiency: The SHG efficiency of solution grown BCAP was tested by using Nd:YAG laser source. The SHG signal of BCAP was found to be 83. This shows that it is found to 0.56 times SHG efficient than KDP crystals. Nd:YAG laser of fundamental wavelength 1064 nm, was allowed to focused on capillary densely packed with the sample. The signal was collected at 90º to the incident beam using aczerny turner monochromator and a visible photo multiplier tube (Hamamatzu R 2059) and recorded in a digital storage oscilloscope (Tektronix TDS 3000B).

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