

Investigations on Structural, Optical, Vibrational and Dielectric properties of 2A5CB single crystals

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Abstract - Good quality single crystals of 2-chloro 5-bromo benzophenone (2A5CB) are grown by slow evaporation solution growth technique. Powder X-ray diffraction studies confirmed the high crystalline nature of the grown crystals and it is in monoclinic crystal system with cc space group. The candidate crystal shows wide transparency window in UV-Vis region. Optical band gap of the grown crystal is found as 3.5 eV using Tauc's plot. Various functional groups present in the sample are learnt by FT-IR studies. SHG behaviour of the material has been confirmed from the output of intense green light emission ($\lambda = 532$ nm) from the crystal. High dielectric constant and dielectric loss at low frequency signifies the presence of charge polarization in 2A5CB molecule.

I. INTRODUCTION

Photonics is playing an ever-increasing role in today's technology by efficiently replacing electronics in electro optic devices. In this context, researchers have been focusing on the search for materials with large optical nonlinearities and for their application in the fields of high speed data transmission, processing and storage [1,2]. Organic molecules are promising candidates since their properties can be custom-tailored, and their dielectric constants and refractive indices are much smaller than those of the most common inorganic molecules. Recently, the possibility of modulating NLO properties at the molecular level using molecules which respond to electrochemical or chemical inputs such as protons or metal cations has been explored [3, 4]. In the systems of donor- π -acceptor type, interaction with a cationic species alters the electron density of the terminal sites, resulting in a modulation of the internal charge transfer character of the molecule which leads to a change in the optical response [4, 5]. There have been several reports of modulation of the two-photon absorption and fluorescence properties of linear chromophores upon cation binding or at the terminal donor substituent. This manuscript deals with the investigations on structural spectral optical and dielectric properties of 2A5CB single crystals.

II. SYNTHESIS AND GROWTH

The commercially available AR grade 2A5CB (Merck) ($C_{13}H_{10}ClNO$) was purified by repeated recrystallization process using ethanol. A volume of 100 ml of ethanol was taken in tight container and then the recrystallized salt of 2A5CB was slowly added. The solution was stirred continuously for nearly 7hrs at 30° C. Once the saturation was reached, the equilibrium concentration of the solute was analyzed gravimetrically. The solubility of the synthesized material of 2A5CB was carried out in ethanol by gravimetric method at various temperatures and it is shown in Figure 1. Optically good quality crystal of dimension 20 mm x 2 mm x 4 mm were obtained within a period of 2 weeks. The photograph of as grown 2A5CB single crystal is shown in Figure 2.

III. RESULTS AND DISCUSSIONS

Powder X-ray diffraction studies

The powder X-ray diffraction was employed to confirm the crystal cell parameters. The powdered sample was scanned in steps of 0.02° over a 2θ range of $10-50^\circ$.

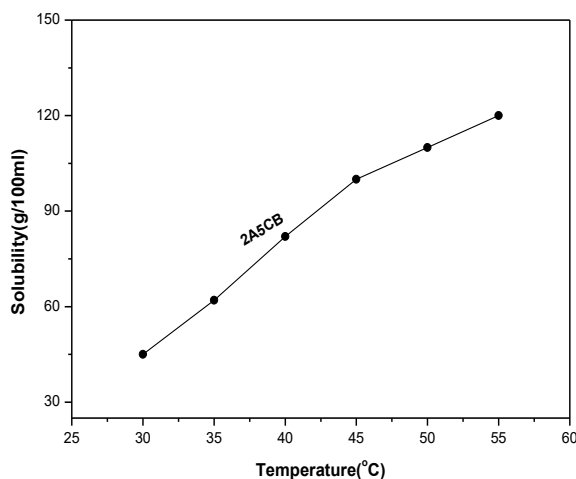


Figure 1 Solubility curve of 2A5CB crystal



Figure 2 Photograph of as grown 2A5CB crystal

All of the observed reflections were indexed, and the unit cell parameters were calculated as $a=9.7403\text{\AA}$ $b=19.005\text{\AA}$ $c=24.789\text{\AA}$. It is also confirmed that the grown crystal belongs to monoclinic crystal system with cc space group. X-ray diffraction pattern of 2A5CB is shown in Figure.3.

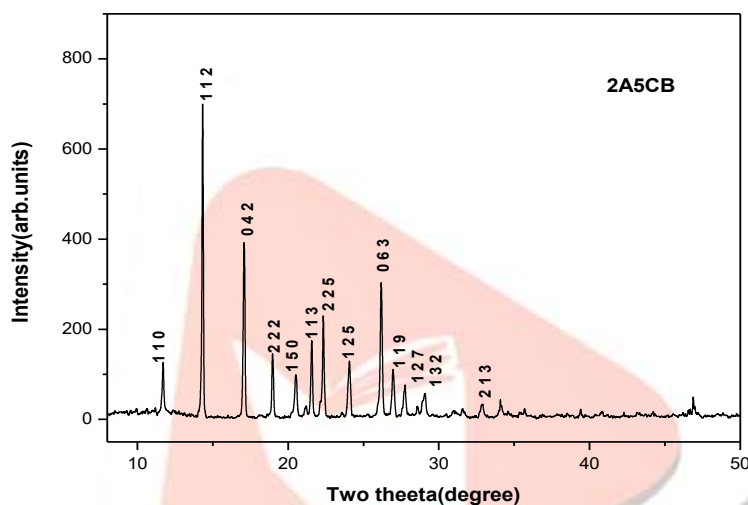


Figure 3 XRD pattern of 2A5CB single crystal

UV-Vis-NIR spectra and Band gap

The optical absorption plays an important role in identifying the potential of the NLO material. Materials having wide absorption window with reduced absorption around the fundamental and second harmonic wavelength are of greater utility for NLO applications. Optical absorption data were taken on these polished crystal samples of about 4 to 6 mm thickness using a Varian carry 5E model dual beam spectrophotometer between 200 – 2000 nm. The absorption is found to be minimum in the entire UV–visible region, and the UV cutoff wavelength of 2A5CB is below 300 nm hence it can be used as a potential material for SHG. The nature of optical transmission depends on optical band gap of the material and it can be calculated with tauc's plot a function of absorption coefficient. The graph representing $(\alpha h\nu)^2$ against $h\nu$ may be resolved into two straight line portions. The straight line obtained at lower photon energies corresponds to phonon absorption process and cuts the energy axis at a value equal to $(E_g - E_p)$ where E_p is the phonon energy. The other line, which represents the dependence in the high energy range, corresponds to a phonon emission process and cuts the energy axis at a value of $(E_g + E_p)$. Extrapolating the graph to $(\alpha h\nu)^2 = 0$ axis yields the optical band gap value of the given material. The band gap of the grown crystal is found as 4.4eV and it is shown in figure. 5.

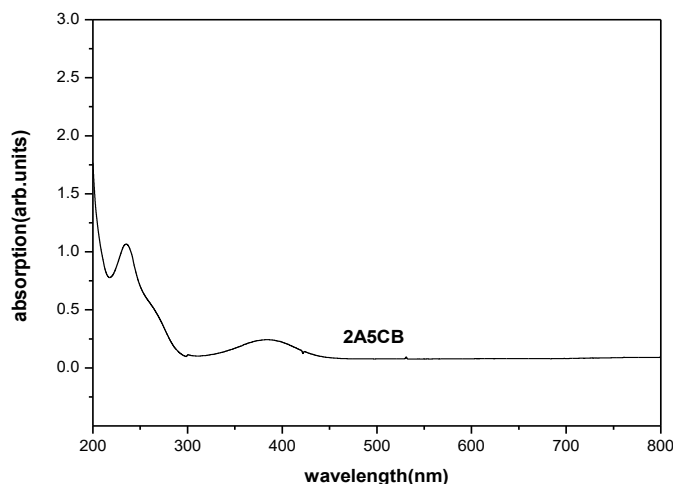


Figure 4 Optical absorption spectrum of 2A5CB single crystal

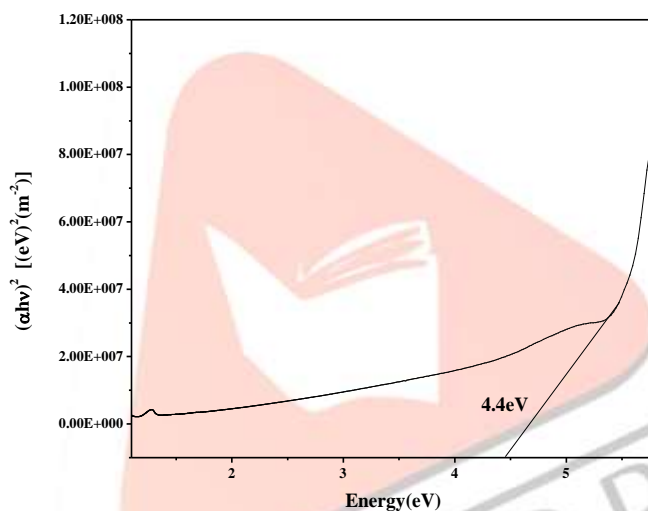


Figure 5 Energy band gap of 2A5CB

FT- IR spectra

FT-IR spectrum of the grown crystal was recorded in the range 400 cm^{-1} to 4000 cm^{-1} , using KBr pellet technique on BRUKKER IFS FT-IR Spectrometer. Figure 6 shows the recorded FT-IR spectrum of the 2A5CB single crystal.

C-Cl Vibrations

In the lower region, C–Cl stretching vibrations appear at $760\text{--}505\text{ cm}^{-1}$ and C–Cl deformation vibrations appear in the region $420\text{--}250\text{ cm}^{-1}$ [6]. Compounds with more than one chlorine atom exhibit very strong bands due to the asymmetric and symmetric stretching modes. Vibrational coupling with other groups may results in a shift in the absorption to as high as 840 cm^{-1} . For simple organic chlorine compounds, C–Cl absorption is in the region $750\text{--}700\text{ cm}^{-1}$ [7]. The sharp peak at 702 cm^{-1} in FT-IR spectrum is due to C–Cl stretching vibrations. The shifts to lower frequencies of 2A5CB, is due to the greater electro negativity of chlorine as compared with carbon atoms. Thus, chlorine atom acquires a small negative charge, and the carbon atom a small positive charge. The inductive effect of chlorine attracts electrons from C–Cl bond, which increases the force constant and leads to an increase in the absorption frequencies. The band at 664 and 646 cm^{-1} is assigned for C–Cl in-plane bending, 520 and 470 cm^{-1} is for out-of-plane bending vibrations in FT-IR vibrational spectrum.

C-H Vibrations

In aromatic compounds, the carbon–hydrogen stretching vibrations normally occur at $3100\text{--}3000\text{ cm}^{-1}$. These vibrations are not found to be affected due to the nature and position of the substituent. Most of the aromatic compounds have nearly four infrared peaks in the region $3080\text{--}3010\text{ cm}^{-1}$ due to ring C–H stretching bands. The infrared peaks identified at 3313 cm^{-1} in the FT-IR spectrum of the 2A5CB shall be due to C-H stretching vibrations. The peak at 1463 cm^{-1} is occurring due to the effect of C–H in-plane bending vibrations. A peak at 1359 cm^{-1} is assigned to C-H out of plane bending mode. Thus the candidate material exhibits a prominent C-H vibration which reveals the high Organic nature.

C – C Vibrations

The ring C=C and C-C stretching vibrations, known as semicircle stretching occurs in the region $1625\text{--}1400\text{ cm}^{-1}$ and $1380\text{--}1280\text{ cm}^{-1}$. Experimental spectrum shows a peak at 1535 cm^{-1} which is due to C=C stretching vibrations. The actual positions of C-C stretching modes are determined not so much by the nature of the substituents but by the form of substitution around the ring. C-C stretching is observed at 1611 cm^{-1} and 801 cm^{-1} from FT-IR analysis for the candidate molecule. The in-plane deformations are at higher frequencies than the out-of-plane vibrations. For this title molecule C-C in plane bending vibrations are observed at 893, 824 cm^{-1} respectively and out of plane bending is at 763 cm^{-1} .

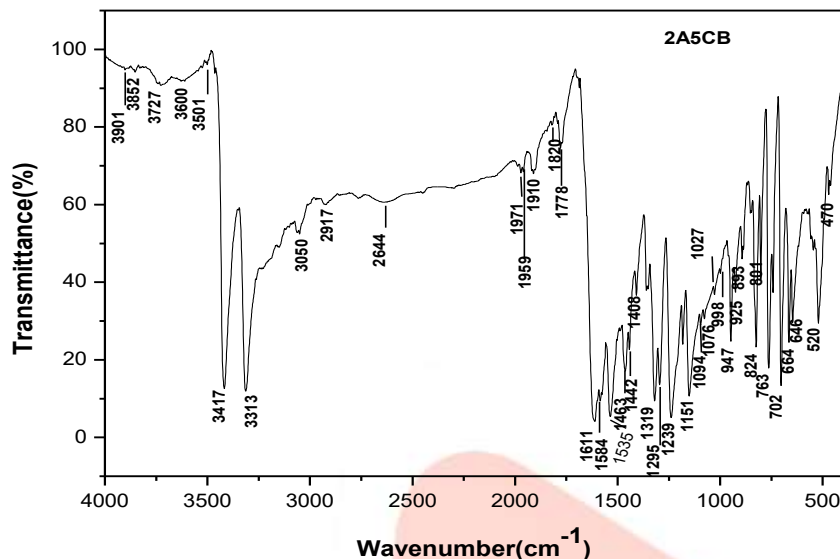


Figure 6 FT-IR Spectrum of 2A5CB single crystal

SHG in 2A5CB crystal

The second harmonic generation behavior of the powdered material is tested using Kurtz and Perry method [8]. A high-intensity Q switched Nd: YAG laser ($\lambda = 1064\text{ nm}$) with pulse duration of 7 ns and frequency repetition of 10Hz is passed through the sample. The SHG behavior is confirmed from the output of the laser beam having the bright green emission ($\lambda = 532\text{ nm}$) from the specimen. The second harmonic signal of 1200 mW was obtained for an input energy of 3.0 mJ/ pulse, while the standard KDP give a SHG signal of 350 mW for the same input energy. KDP sample was used as the reference material. Thus the efficiency is 3.4 times higher that of KDP.

Dielectric Studies

The dielectric study on the 2A5CB single crystal was carried out using the instrument, HIOKI 3532-50 LCR HITESTER. A sample of dimensions about $4 \times 2 \times 1.2\text{ mm}^3$ having silver coating on the opposite faces were placed between the two copper electrodes and thus a parallel plate capacitor was formed. The variations of dielectric constant and dielectric loss as a function of log frequency are illustrated in Figs 7 and 8. It is observed that the dielectric constant decreases with increase in frequency. The decrease is rapid in the low frequency range and then it starts decreasing very slowly. In high frequency region both dielectric constant and dielectric loss are fairly remaining constant. The high dielectric constant at low frequency is due to better orientation of dipoles in the molecules. With increase in frequency the dipoles oscillate in resonance to oscillating field. Broadly speaking, the graphs exemplify the fact that the dielectric constant and the dielectric loss are both sensitive to frequency. The low value of dielectric loss indicates that the crystal has lesser defects, which is a desirable property for NLO applications.

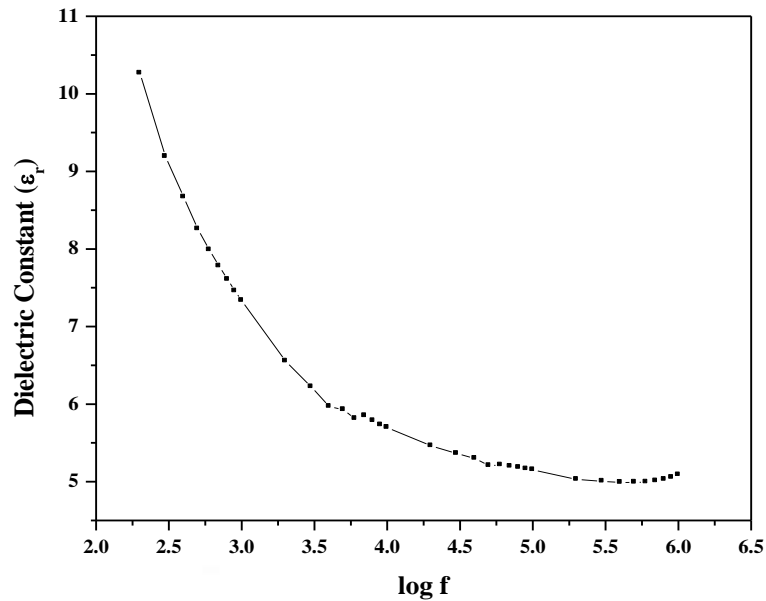


Figure 7 Variation of dielectric constant of 2A5CB

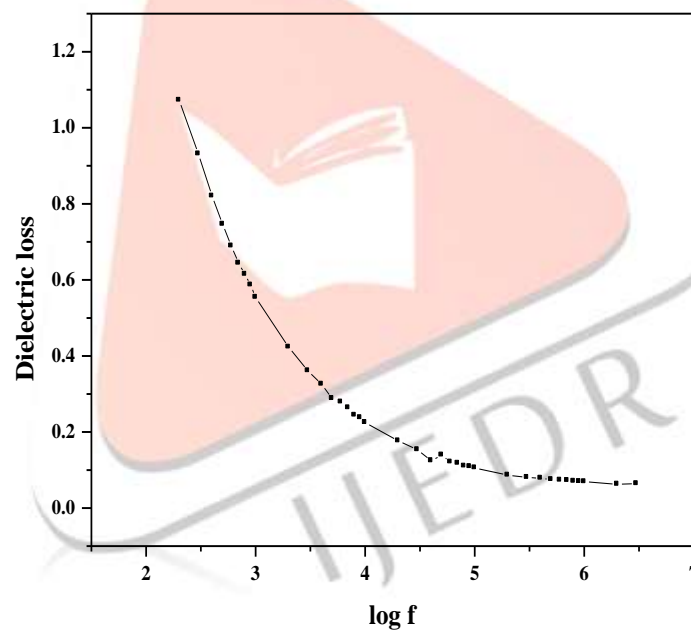


Figure 8 Variation of dielectric loss of 2A5CB

IV. CONCLUSION

Good quality single crystals of 2A5CB are grown successfully by slow evaporation technique. The crystalline nature of the grown crystal is confirmed by powder XRD studies. Optical absorption studies of 2A5CB shows a wide transparency window in the UV-Vis-NIR region and makes the crystal suitable for NLO device fabrication. Tauc's plot enabled optical band gap is calculated as 4.4 eV. Vibrational spectral analysis confirmed the presence of various functional groups in the sample. Second Harmonic Generating efficiency of the candidate material is found as 3.4 times higher than KDP. Dielectric behavior of the sample is analyzed. It is found that dielectric loss and dielectric constant decreases with increase in frequency. 2A5CB single crystal is a suitable material for NLO applications.

V. REFERENCES

- [1] H. S. Nalwa, S. Miyata, Nonlinear Optics of Organic Molecules and Polymers, CRC Press: FL, 1997.
- [2] K. Clays, K. Wostyn, G. Olbrechtes, A. Persoons, A. Watanabe, K. Nogi, X. Duan, S. Okada, Oikawa, H. Nakanishi, H. Bre´das, "Fourier analysis of the femtosecond hyper-Rayleigh scattering signal from ionic fluorescent hemicyanine dyes" J. Opt. Soc. Am. B., Vol. 17, pp 256, 2000.

- [3] I. Asselberghs, K. Clays, A. Persoons, M. D. Ward, McCleverty., "Switching of molecular second-order polarisability in solution" J. J. Mater. Chem., Vol. 14 ,pp 2831, 2004
- [4] K. Rurack, "Flipping the light switch 'ON' – the design of sensor molecules that show cation-induced fluorescence enhancement with heavy and transition metal ions" Spectrochim. Acta, Part A., Vol.57, pp 2161, 2001.
- [5] Verbiest T, Houbrechts S, Kauranen M, Clays C, Persoons A., "Second-order nonlinear optical materials: recent advances in chromophore design" J. Mater. Chem., Vol. 7,pp.2175, 1997.
- [6] Tonannavar, Jayashreeyeni, "Vibrational spectra, normal modes, *ab initio* and DFT calculations for 6-Chloro- and 7-Chloro-4-bromomethylcoumarins" Spectrochim. Acta A Vol. 77,pp.351, 2010.
- [7] Krishnan A.R., H. Saleem, S. Subashchandarabose, N. Sundaraganesan, Sebatain S, "Molecular structure, vibrational spectroscopic (FT-IR, FT-Raman), UV and NBO analysis of 2-chlorobenzonitrile by density functional method" ,Spectrochim. Acta A Vol.78, pp.582, 2011.
- [8] S.K Kurtz and T.T. Perry, "A Powder Technique for the Evaluation of Nonlinear Optical Materials", J. Appl. Phys., Vol. 39, p.3798, 1968.

