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Growth and Characterization of an organic metal doped 4-chloro-4'-chlorobenzylidene aniline Nonlinear Optical Material

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ABSTRACT

Optically good quality single crystals of metal doped 4-chloro-4'-chloro benzylidene aniline was grown by slow evaporation method, to improve the optical properties of the pure materials. The effects of metal doping on the growth, structural and optical properties of the grown crystal have been investigated. From powder x-ray diffraction study, the cell parameters were determined. The presence of various functional groups in the grown compound was identified by Fourier transform infrared spectrum. The optical transparency of the grown crystals was studied by using UV-VIS-NIR spectroscopy. Fluorescence studies also recorded for the grown crystal which confirms aromatic functional groups with low energy in the compounds. The nonlinear optical activity of the grown crystals was obtained by using Kurtz-Perry powder technique.

Key words: Fluorescence, FTIR, Powder XRD, NLO, UV-VIS-NIR.

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I. INTRODUCTION

Materials with large nonlinear optical susceptibilities are of current interest in the area of harmonic generation and optical modulation. In recent years, some polar organic crystals, which form a non-centrosymmetric structure exhibit second-order nonlinear optical property that far surpassed those of the conventional materials has led to the synthesis and evaluation of a wide range of potentially useful solids [1-2]. The extensive research of new nonlinear material is an important task because of their application in telecommunication for efficient signal processing and optical information storage devices. Organic molecules with significant nonlinear optical activity generally consist of a π – electron conjugated structure. The conjugation π -electron provides a pathway for the entire length of conjugation under the perturbation of an external electric field. Fictionalization of both ends of the π bond systems with appropriate electron donor and acceptor group can increase the asymmetric electronic distribution in either or both the ground and excited states, thus leading to an increased optical nonlinearity [3]. Among many organic compounds reported for the SHG benzylidene aniline derivatives. In the same way organometallic materials have the combined nature of chemical flexibility of organic materials and mechanical strength of inorganic materials. These materials exhibit high nonlinear optical properties [4].In this work we introduce a metal ion zinc (Zn) to the benzylidene aniline derivative and the grown crystals were subjected to powder XRD, FTIR, UV-Visible, fluorescence and powder SHG studies and the results were reported.

II. MATERIAL SYNTHESIS AND CRYSTAL GROWTH

The commercially available 4-chloro aniline and 4-chloro benzaldehyde (AR grade) salts are taken in equal molar ratio have been used to synthesize the 4-chloro-4'-chloro benzylidene aniline single crystals. All the preparation and growth process have been carried out in a solvent of ethanol by condensation process. After that a 5% of Zn metal powder was added to the solution and the reaction mixture was refluxed about 8 hours and the solution was filtered using Whatman filter paper. The final product was filtered by Whatman filter paper and kept in a petri dish. The solution was placed in undisturbed position. After two weeks, good transparency, well defined tiny crystals have been obtained by slow evaporation technique. Good quality and defect-free seed crystals were used to grow bulk-size crystal. A good quality highly transparent and full-face crystalsof ZCCBA wasobtainedwithin four weeks.

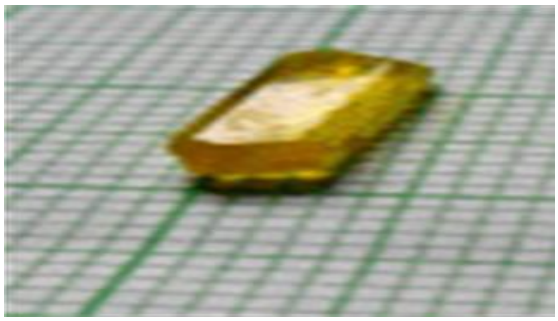

Fig.1 Grown crystal of CCAB

III. RESULT AND DISCUSSION

3.1. X-ray Diffraction Analysis

The grown crystals were characterized by powder x-ray diffraction. The sample ZCCBA was scanned in the range 10º-80º at scan rate of 2θ min^{-1}. The powder diffraction pattern of ZCCBA was shown in Fig. 2. The well-defined Bragg's peak reveals the high crystalline nature of the crystal. It reflects the good crystallinity of the grown crystal. The lattice parameters were calculated using TREOR programme, coincides with single crystal XRD results already reported by Jothi et al [5].

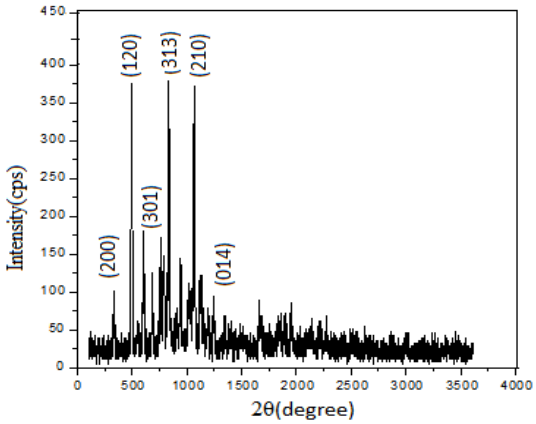

Fig.2 Powder XRD patterns of CCAB

3.2. FTIR Spectral Analysis

A Perkin Elmer-Paragon, Fourier Transform Infrared (FTIR) spectrometer was used to record the FTIR spectrum of ZCCBA in the range of 400 - 4000 cm^{-1} by using the KBr pellet technique. The FTIR spectrum of ZCCBA was shown in Fig. 3 and the functional groups were analysed taking in to account of the molecular structure of the material. The very broad peak at 517.66 cm^{-1} corresponds to strong N-H stretching vibration. Hence the band obtained at 1296.26 cm^{-1} confirms the formation C-N stretching vibration. The band at 1589.64$cm^{-1}$is attributed to the N-H stretching vibrations in the compound. A weak Peak at 537.49 cm^{-1} is assigned to C-Cl bond assignments of ZCCBA. The major variation of frequencies of carboxylic group and NH3, clearly confirms the presence of Zinc metal ions in the grown ZCCBA materials [6-7].

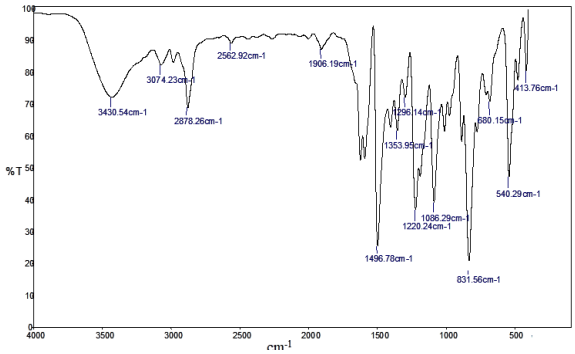

Fig.3 FTIR Spectrum of ZCCBA

3.3. UV- VIS - NIR Studies

The optical transmission spectrum of ZCCBA was recorded using Perkin Elmer Lamda 35 spectrophotometer in the wavelength range from 1100 nm to 230 nm. The UV transmission spectrum was shown in Fig. 4.

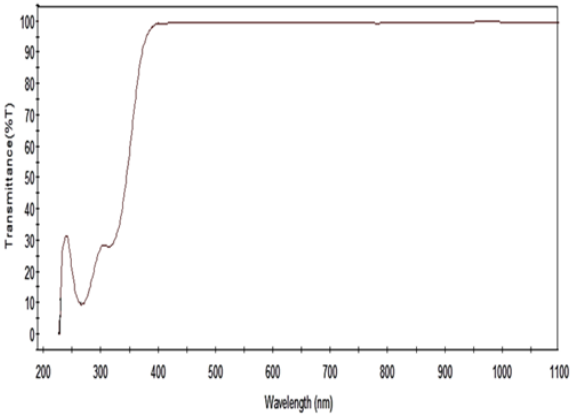

Fig.4 UV-Transmission Spectrum of ZCCBA

The transmittance between 200 -390 nm was gradually increased and the upper cut off wavelength was found at 270 nm and have maximum transmission 99% above 390 nm. The absence of absorption in the visible region confirms to the colourless nature of the crystal and was an advantage as it was the key requirement for materials used in optoelectronics applications [8]. The optical band gap of ZCCBA was calculated as 4.59 eV.

3.4. Fluorescence Spectrum

Fluorescence generally found in compounds containing aromatic functional groups with low energy $\pi \rightarrow \pi^*$ transition levels. Compounds containing aliphatic and alicyclic carbonyl structures or highly conjugated double-

bond structures exhibit fluorescence. The emission spectrum of ZCCBA was recorded using JOBINVYON FLUROLOG 3 Spectrofluorometer in the range 200-800 nm. The fluorescence spectrum of ZCCBA crystals was show in Fig.5,the sharp band at 550.48 nm is obtained in the emission spectrum. The emission was assigned to the electronic transition from π* antibonding molecular orbital to π bonding molecular orbital of the grown crystals. The higher intensity ratio indicates purity and perfect crystallinity of the title compound. A peak at about 550 nm indicates that ZCCBA crystal has a green fluorescence emission.

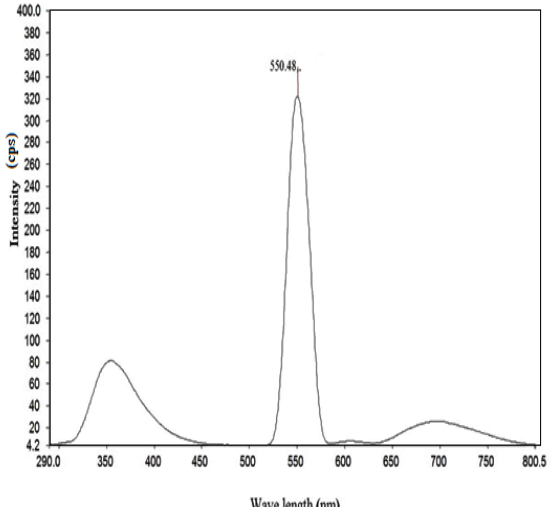

Fig.5 Fluorescence Spectrum of ZCCBA

3.5. SHG Efficiency test

The NLO efficiency of the ZCCBA crystal was estimated by using Kurtz and Perry technique. The fundamental beam of Q-switched, mode locked Nd: YAG laser operating at 1.06 nm and generating pulses of duration 35 ns and 10 Hz repetition rate is focused on to the powdered sample. The SHG was confirmed by emission of green radiation from the sample. The well-known NLO crystals are taken as the reference materials and the conversion efficiency of ZCCBA was compared. The SHG efficiency was found to be 2.1 times greater than that of the standard KDP crystal. The second order optical properties of organic crystals can be greatly enhanced by using metal ions.

IV. CONCLUSION

The organic crystal ZCCBA was synthesized by condensation process and grown from slow evaporation method at room temperature using ethanol as solvent. The various characterization techniques have been employed to confirm the presence of zinc metal ion in grown ZCCBA crystals such as powder XRD, FT-IR and UV-VIS-NIR and fluorescence studies. The crystalline nature of the grown material ZCCBA are confirmed from the sharp well-defined peaks by powder XRD diffraction. The recorded FTIR spectrum of the grown material confirms the functional groups present in the compound in the wavelength range of 400 - 4000 cm^{-1}. The UV-VIS-NIR spectrum of grown crystals exhibit the very low absorption property in the visible region suggests its suitability for the fabrication of opto electronics devices. The fluorescence spectrum of ZCCBA crystals exhibit fluorescence and the grown crystals have green emission of radiation.

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