Growth and characterization of nonlinear optical Bis-(L-Tyrosinato) Cupric acetate (BLTC) single crystals

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Abstract: Bis-(L-tyrosinato) Cupric acetate (BLTC) material was synthesized and single crystals of BLTC were grown by slow evaporation method. The grown crystal has been subjected to single crystal X-ray diffraction to determine the unit cell dimensions. BLTC crystal was also characterized by recording the powder X-ray diffraction patterns and by identifying the diffracting planes. The functional groups and molecular structure of the title compound are confirmed through Fourier transform Infrared (FT-IR) spectrum. The Hydrogen and Carbon environment of the grown crystals were analyzed by FT-NMR spectrum. The transparency nature of the BLTC crystal was determined using UV-Vis-NIR spectrophotometer. The thermal property of BLTC was established through thermo gravimetric (TG) and Differential thermal analysis (DTA) technique. The second harmonic generation (SHG) of the material was investigated by Kurtz and Perry powder technique and was observed to be greater than that of KDP.

Keywords-- ***crystal growth, nonlinear optical material (NLO), nuclear magnetic resonance, slow evaporation, second harmonic generation (SHG), X-ray diffraction***

I. INTRODUCTION

Nonlinear optics is one of the foremost eye-catching fields of modern research in view of the applications in the areas such as optical switching, optical logic, optical interconnections, bio Photonics and frequency converters in generating lasers at new optical frequencies which is impractical with the existing lasers [1], [2], [3]. In addition to this NLO materials have been using for industrial applications. The recent research in Pharmaceutical industry shows bringing new, higher quality drugs to the market in reduced time is possible because of the NLO studies. [4], [5]. Materials exhibiting large non linearity remains very active in research both basic and applied sciences [6]. The assortment of material may depend not only on laser conditions but also on the physiochemical properties such as molecular nonlinearity, transparency, and conversion efficiency and laser damage threshold [7], [8]. In metal-organic compounds, the position of metal cores can commonly perform as donors and the bridging moiety in D–π–A arrangement and the metal–ligand bond is projected to display large molecular hyperpolarisability because of the shift of electron density between the metal atom and the conjugated ligand structure [9]. Amino acids, which plays a very important role in nonlinear optical applications, it contains amine ($-NH_2$) and carboxylic (-COOH) functional groups along with a side chain exact to each amino acid, thus making them ideal candidates for NLO applications. Amino acids, when added as impurities, have improved materials properties. Due to this reason researchers have been paying attention amino acid based non-linear optical materials [10], [11]. L-Tyrosine is one of the amino acids and its hydrogen halides are created to have promising NLO properties and form coordination compounds with metal ions using carboxylate, amino and hydroxyl groups [12]. The aromatic arm of L-Tyrosine and the π cation interaction between metal cations Cu(II) produces asymmetric domain about Cu(II) as core. The asymmetric induction is due to the intermolecular π cation interaction between Cu(II) and indole ring [13]. The present investigation discusses the growth of BLTC crystals grown by slow evaporation solution growth technique. The grown crystal (BLTC) was subjected to various characterization studies such as single crystal XRD, FTIR, UV-VIS-NIR, Thermal, NMR and NLO test.

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II. EXPERIMENTAL ANALYSIS

A. Crystal growth of BLTC

Single crystals of Bis-(L-Tyrosinato) Cupric acetate (BLTC) were grown by taking equimolar ratio of highly pure L-Tyrosine(AR) grade and Cupric acetate(AR) grade. Deionized water was used as a solvent to crystallize BLTC single crystal. The mixture was placed in a magnetic stirrer and stirred about 14 hours. Extensive time stirring was done for the homogeneous mixing of the mixture. A small pale blue single crystal, free of macro defects obtained from the saturated solution of BLTC, was selected as a seed crystal. Mother solution of BLTC was saturated at 40^{o}C and seed was introduced into the saturated solution placed in a constant temperature bath (±1^{o}C) and the solution was maintained in the temperature for 24 hours. The solution was then allowed to cool at the rate of 1^{o}C per day under constant stirring. Good pale blue single crystals were harvested in 40 days. The as grown BLTC crystal shown in Figure 1.

$$Cu(CH_3COO)_2 + C_9H_{11}NO_3 \Rightarrow Cu(C_9H_{10}NO_3)_2$$

B. Characterization

The grown single crystals of Bis-(L-Tyrosinato) Cupric acetate (BLTC) have been analyzed by different characterized techniques. The grown crystals were confirmed by single crystal X-ray diffraction analysis using ENRAF NONIUS CAD-4 diffractometer with MoK_{α} radiation (λ = 0.71073 Å). FT-IR spectrum was recorded in the range of 4000- 400 cm^{-1} using a BRUKER IFS66 V Spectrophotometer by KBr Pellet technique. The optical properties of the grown crystal were examined between 200-800 nm using a VARIAN CARY 5E Spectrophotometer. The thermal analysis of the BLTC crystal was carried out in the range from 20-800 ^{o}C using the instrument NETZSCH-STA 409 PC Thermal analyser at a heating rate of 10 ^{o}C min^{-1} in nitrogen atmosphere. The FT-NMR spectra were recorded using JEOL-GSX 4000 NMR spectrometer operating at 300 MHz with DMSO as solvent. The Kurtz and Perry powder method is used to calculate the efficiency of NLO property.

III. RESULT AND DISCUSSION

A. X-ray diffraction study

To confine the crystallinity of grown BLTC crystals and also the universal parameters of BLTC, X ray diffraction analysis were carried out using ENRAF NONIUS CAD-4 automatic X ray diffractometer with a incident MoKα radiation. It was found that the grown BLTC crystal belongs to orthorhombic structure with the space group $P2_12_12_1$. The calculated lattice parameters are a = 13.201 Å, b = 5.923 Å, c = 22.311 Å and V = 1744.486 (Å)^3, which are in very good agreement with the reported values [14]. X- ray powder diffraction has been widely used in past as a standard technique for qualitative and quantitative phase analysis [15]. The powder sample of BLTC was scanned over the range 10°-70°at a rate of 1° min^{-1} using a RICH-SAIFERT, 2002 DLX model powder x ray diffractometer with Cu Kα (1.54289 Å) radiation. From the X-ray diffraction pattern all the observed reflections were indexed as shown in Figure 2 and the required cell parameters were calculated using 2θ values of this reflection with the help of PROSZKI software package [16].

B. FT-IR analysis

The Fourier transform infra-red (FT-IR) analysis is an important study to analysis quantitatively the presence of various functional groups and structure of the compound. FT-IR spectrum of BLTC is shown in Figure 3. FT-IR spectrum of the complex shows a strong broad band at 3264cm^{-1} is due to –OH stretching frequency of carboxyl and N-H group. The appearance of two absorption bands at 1584 cm^{-1} and 1415 cm^{-1} are due to NH_2 bending of amine and CH_2 bending respectively. The peak at 1737cm^{-1} is due to carboxyl stretching of –COOH group of tyrosine moiety.

C. NMR studies

The investigation of ^{1}H NMR and ^{13}C NMR Spectral studies have been carried out using JEOL-GSX 4000 NMR spectrometer operating at 300 MHz with DMSO as solvent. The ^{1}H and ^{13}C NMR spectrum is shown in Figure 4(a) and 4(b). In proton NMR the signal at δ = 9.06 ppm and δ = 8.71 ppm are due to proton with phenol and indole ring respectively. The nonequivalent triplet peak at δ = 4.14 ppm is due methane. The quartet signal at δ = 3.42 ppm and δ = 3.17 ppm due to methylene. In ^{13}C NMR spectra the signal at δ =37.3 ppm and δ = 56.7 ppm is assigned to carbon bonded with aliphatic. The signal at δ =155.7 ppm, δ =129.2 ppm and δ =115.8 ppm are due to carbon in benzene ring.

D. UV-VIS-NIR Spectrum

The UV-Vis-NIR spectrum of BLTC is shown in Figure 5. The UV–Vis spectral studies are usually employed to conclude the transparency of a crystal which is key requirement for NLO applications. The optical absorption spectrum of BLTC crystal was recorded in the range from 200 - 800 nm using UV-Vis-NIR spectrophotometer. The spectra of the BLTC in water exhibit high intense π-π* electron transition in the UV region around 330 nm, a low intensity d-d electron transition band around 647 nm [17]. The UV cutoff wavelength is found to be less than 270 nm. The transmittance is maximum in the wavelength region between 330nm- 640nm.

E. Thermal analysis

Thermo gravimetric and differential thermal analysis (TG/DTA) of BLTC is shown in Figure 6. The thermal studies were done using PERKIN ELMER DIAMOND

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instrument at a heating rate of 10 °C min^{-1} in the temperature range of 20-800 °C. The resulting TGA; DTA shows that the sharp weight loss of the material starts around 154 ^{o}C, this weight loss is about 28%. It is interesting to note that the DTA of the complex shows characteristic endothermic at the same temperature (154 ^{o}C), this can be attributed to the fact that, phase transition in the temperature range. The crystal is completely free of any crystallized water or physically adsorbed water on the surface. Further this observation was attested by absence of band in the region of 3400 cm^{-1} to 3500 cm^{-1} confines the absence of the water molecule. There is a major weight loss at 295 ^{o}C. So it may be concluded that the complex is stable up to 154 ^{o}C, melting transition were not observed within the measured range.

F. NLO Test

The second harmonic generation efficiency was measured by following the Kurtz and Perry powder method [18]. The title crystal was grounded into uniform powder and then packed in a micro-capillary of uniform bore and exposed to a Q-switched Nd:YAG laser beam of wavelength 1064 nm. The second harmonic signal was confirmed from the emission of green radiation of wavelength 532 nm from the crystalline powder and detected by a photo multiplier tube and compared with standard KDP. It is found that SHG efficiency of BLTC is 1.2 times that of standard KDP.

IV. CONCLUSION

Single crystals of Bis-(L-Tyrosinato) Cupric acetate (BLTC) were grown by slow evaporation method. The powder XRD and single crystal XRD confirmed the crystal structure of BLTC. The various functional groups and molecular structures present in the grown crystals (BLTC) were identified by recording FT-IR and Hydrogen and Carbon NMR spectral analysis. The optical absorption spectral analysis reveals that the crystal is transparent in the entire visible region with a cut-off wavelength of 330 nm. A sharp endothermic peak at 154 ºC corresponds to the melting point of the title compound. Second harmonic generation (SHG) studies reveal that BLTC crystal is a promising candidate for NLO applications.

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FIGURES

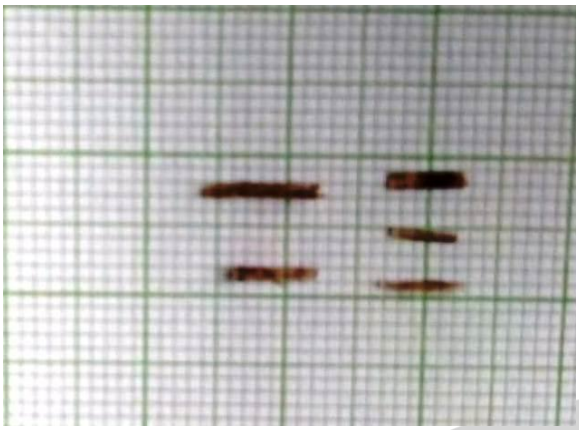

Figure 1. As grown crystal of BLTC

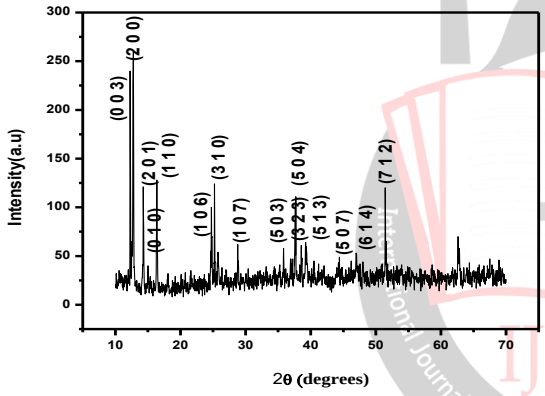

Figure 2. X-ray powder diffraction pattern of BLTC

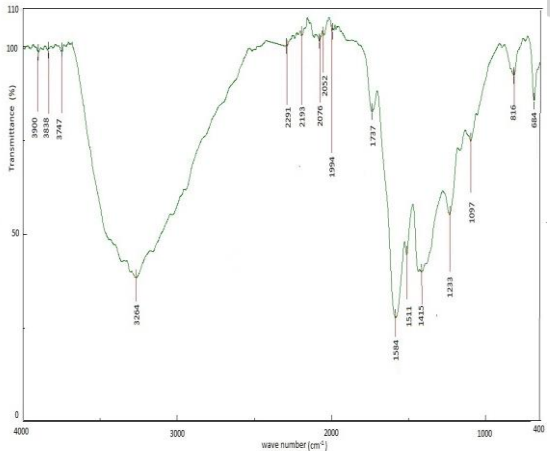

Figure 3. FT-IR spectrum of BLTC

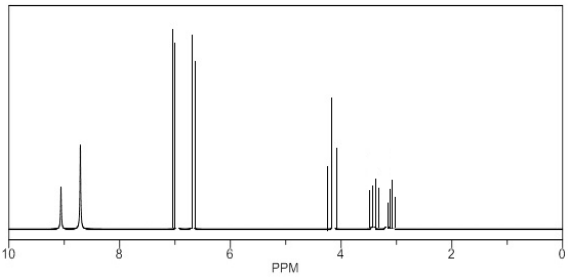

Figure 4(a). ^{1}H NMR spectrum of BLTC

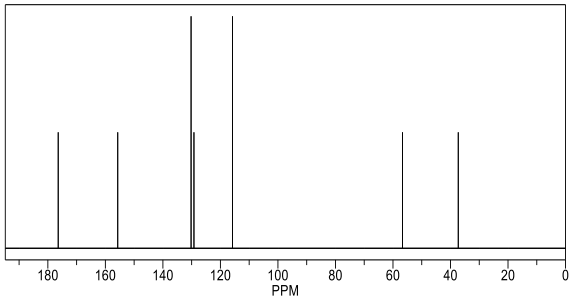

Figure 4(b). ^{13}C NMR spectrum of BLTC

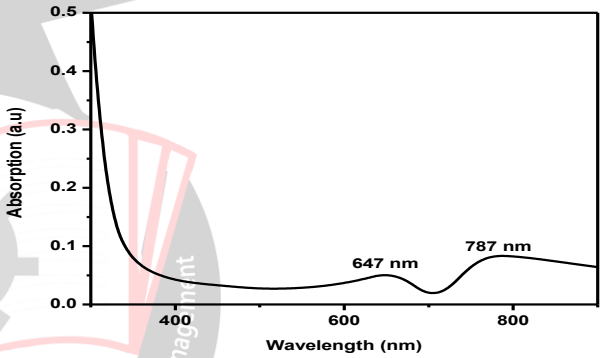

Figure 5. Optical absorption spectrum of BLTC

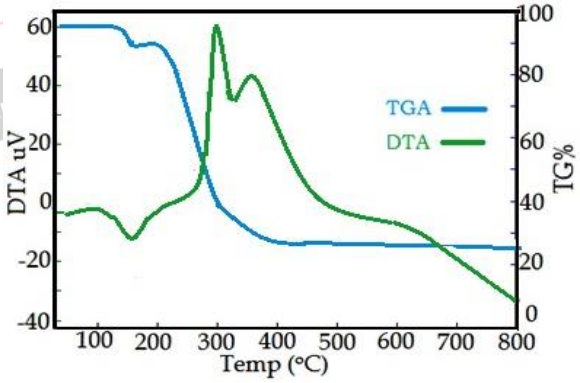

Figure 6. TG,DTA curve of BLTC

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