

Growth and Characterisation of new Semi Organic Crystal Bisthiourea Calciumacetate

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Abstract: A novel bisthiourea calciumacetate was grown from saturated solution by slow evaporation solution growth technique at ambient temperature. The stoichiometric ratio of the compound was confirmed by elemental analysis. The crystallinity of the compound was confirmed by the sharp and well defined Bragg peaks observed in the powder X-ray diffraction pattern. The UV-visible absorption study was studied to ascertain the optical property of the compound. The thermal stability and decomposition pattern of the compound were formulated using TG-DTA studies. The heating and cooling cycles observed in differential thermal analysis (DSC) indicates that the compound shows first order phase transition. The FTIR spectroscopic technique was used to find out the various characteristic absorption bands present in the compound. The number of protons environment of the compound was confirmed by the NMR spectral studies. The second harmonic generation (SHG) efficiency of the compound indicates that the compound has SHG efficiency twice than that of standard potassium dihydrogen phosphate (KDP).

I. Introduction

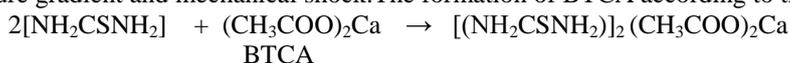
Recent trends nonlinear optics is playing a major role in the emerging photonic and optoelectronic technologies. New nonlinear optical (NLO) frequency conversion materials have a significant impact on laser technology, optical communication and optical data storage. Second order nonlinear optical (SONLO) materials have recently attracted much attention because of their potential applications in emerging optoelectronic technologies [1-5]. Thus the search for new NLO materials has been the subject of intense research. Materials with large second-order nonlinearities, large optical transmission window and stable physicochemical performance are needed for various applications [6]. Much recent work have demonstrated that organic crystals can have very large nonlinear susceptibilities compared with inorganic crystals, but their use is impeded by low optical transparency, poor mechanical properties, low laser damage threshold and the inability to produce large crystals. Purely inorganic nonlinear optical (NLO) materials typically have excellent mechanical and thermal properties with relatively modest optical nonlinearities because of the lack of extended p-electron delocalization [7]. Under this circumstance, the quest for NLO materials is concentrated on a new class of materials called semiorganic crystals with high second harmonic generation (SHG) coefficients as well as stable physicochemical properties [8-11]. Due to their large nonlinearity, high resistance to laser induce damage, low angular sensitivity and good mechanical hardness, the semiorganic materials have the potentials for combining the high NLO property and chemical flexibility of organic materials with physical sturdiness and excellent transmittance of inorganic materials. Among the semiorganic NLO materials, metal-complexes of thiourea family have been investigated actively [12-14], and a variety of thiourea metal-complex crystals have been grown [15-18]. With large dipole moment and centrosymmetric nature, thiourea has the ability to form a widespread network of hydrogen bonds [19], which produces excellent noncentrosymmetric complexes such as zinc thiourea sulphate (ZTS), bisthiourea cadmium acetate (BTCA), bis thiourea zinc acetate (BTZA), bisthiourea zinc chloride (BTZC), bisthiourea bismuth chloride (BTBC) and bisthiourea cadmium iodide (BTICI) [20-26]. Motivated by the intriguing properties of this material, an attempt has been made to synthesize and growth of thiourea crystal. These grown crystals are subjected to C H N S analysis, powder XRD, UV, TG, DTA, low temperature DSC, FTIR, NMR and nonlinear optical techniques and the results obtained are reported here and discussed.

II. Experimental Details

2.1 Growth of Single Crystals of Bisthiourea Calciumacetate

Single crystals of bisthiourea calciumacetate (abbreviated as BTCA) were grown by slow evaporation of saturated aqueous solutions at room temperature. Two moles of thiourea and one mole of calcium acetate react to form BTCA crystals. Aqueous solutions containing analytical grades of thiourea and calcium acetate in 2:1 molar ratio respectively were prepared by using triply distilled water. The two solutions were mixed together and stirred well for about 4 h and then resulting solution was filtered through a Whatmann 42 filter paper into a

clean dry beaker. The beaker was covered by an ordinary filter paper. Care was taken to minimize the temperature gradient and mechanical shock. The formation of BTCA according to the following equation.



Bright, transparent and yellow coloured BTCA crystals were obtained. Crystallization took place within 20 to 30 days. The grown crystals were collected from the mother liquid by using well cleaned forceps. The harvested crystals were recrystallized repeatedly to get crystals of good quality. The photograph of BTCA crystal is shown in Fig.1.



Figure1. Photograph of BTCA crystal

2.2 Characterization of Bisthiourea Calciumacetate Crystal

C H N S analysis of BTCA crystal was carried out using ELEMENTAL VARIO EL III MODEL analyzer, (STIC) Cochin. The powder XRD patterns of BTCA crystal were obtained using BRUKER AXS D8 Advance X-ray diffractometer model instrument with Cu K α radiation ($\lambda = 1.54060 \text{ \AA}$) at room temperature. The UV-VIS-NIR spectrum of BTCA was carried out using JASBO V-550 spectrometer. The thermal analysis (TG and DTA) of BTCA were recorded using a PERKIN ELMER DIAMOND thermal analyzer under nitrogen atmosphere. The samples were heated from room temperature to 1020°C at a rate of 10°C per minute. The FTIR spectra of BTCA crystal were recorded using a Perkin Elmer model RX1 instrument. The NMR spectra of BTCA crystal were carried out using Bruker AVIII 500 MHz NMR instrument model. The second harmonic generation (SHG) of the material was carried out using Nd:YAG laser

III. Results And Discussion

3.1 Elemental Analysis

The elemental analysis data obtained for BTCA crystals given in Table1. It is evident that the experimental and calculated percentages of Carbon, Hydrogen and Nitrogen are very close and within the experimental errors. The elemental analysis data of the compound confirms the formation of the compound in the stoichiometric proportion.

Table 1. Elemental analysis of BTCA crystal

S%	N%	H%	C%	Element
22.37	19.58	4.89	16.78	Experimental
22.12	19.35	4.67	16.57	Calculate

3.2 Powder X-Ray Diffraction Method

The powder X-ray diffraction pattern of BTCA is shown in Figure 2. The sharp and well defined Bragg peak at specific 2θ value in the powder XRD pattern confirms its crystallinity.

3.3 Thermal Analysis

3.3.1 Thermogravimetric Analysis

The TG-DTG thermograms of the compound BTCA are shown in Figure 4. The compound was subjected to uniform heating at a heating rate of 10°C per minute at nitrogen atmosphere. The compound BTCA decomposes in single stage when it is heated from room temperature to 1200°C. The compound is found to be stable up to 150°C. Afterwards, it decomposes in a single stage between 170 and 800°C. It is evident that the compound decomposes on heating up to about 800°C. During this portion of heating the entire molecule is decomposed leaving behind the metal, calcium. The experimental weight loss for this portion is 88%. The calculated weight loss is 87%. The close agreement between the experimental and calculated weight losses confirms the formation of the compound. The thermal derivative curve in DTG (solid curve) study conforms to the weight loss pattern in the TG curve. Thus the DTG study confirms the weight losses observed in the TG thermograms.

3.3.2 Differential Thermal Analysis

The DTA curve of the compound BTCA is shown in Figure 5 Two endothermic peaks are observed. The endothermic peaks appear between 170 and 700°C is due to the entire molecule is decomposed leaving behind the metal, calcium.

3.4 Nuclear Magnetic Resonance (NMR) Spectroscopy

3.4.1 ^1H NMR Spectrum

The ^1H NMR spectrum of BTCA is shown in Figure 6. The appearance of two distinct signals in the spectrum indicates two different protons. The NMR the signal at 83.4 ppm is assigned to CH_3 protons. The N-H proton signal appears between 8.5 to 8.4 ppm. The signal at 1.94 ppm is assigned to solvent peak. The TMS signal appears at 0 ppm.

3.5 FTIR Spectrum

The FTIR spectrum of BTCA is shown in Figure 7. The NH_2 stretching vibration is observed at 3285 cm^{-1} . The absorption at 3193 cm^{-1} is assigned to N-H stretching vibration. The C-H stretching vibration is observed at 2751 cm^{-1} . The absorption at 2381 cm^{-1} is characteristic of C-C bond stretching vibration. The combination band and overtone for appear at 2184 cm^{-1} . The NH_2 bending vibration observed at 1880 cm^{-1} . The peak at 1632 cm^{-1} is assign to N-H bending vibration. The stretching vibration of COO^- group appears at 1559 cm^{-1} . The absorption at 1414 cm^{-1} is due to presence of C-N stretching vibration. The N-H rocking vibration is observed at 1106 cm^{-1} . The peak absorbed at 663 cm^{-1} and 448 cm^{-1} are due to C=S stretching vibration and N=C=N bending vibration respectively. This is for thiourea calcium acetate compound.

3.6 Non-Linear Optical Properties

The nonlinear property of the sample was determined by the modified version of the Kurtz and Perry powder technique using a Nd: YAG laser with a pulse repetition rate of 10 Hz working at 1064 nm. The sample was ground into fine powder and it is tightly packed in a micro-capillary tube. It was mounted in the path of the laser beam of 3.1 mJ pulse energy obtained by splitting the original laser beam. The output light was passed through a monochromator transmitting only the second harmonic (green) light at 532 nm. The green light intensity was registered by a photomultiplier tube and converted into an electrical signal. This signal was displayed on the oscilloscope screen. Second Harmonic Generation (SHG) conversion efficiency was computed by the ratio of signal amplitude of the sample to that of the Potassium dihydrogen phosphate (KDP) signal amplitude recorded for the same input powder. The emission of green light from the title sample indicates that the sample shows the second harmonic generation efficiency. The SHG efficiency of the compound may be due to the presence of intermolecular hydrogen bonding in the crystal lattice and also the presence remarkable hyperpolarizability of the title compound.

3.7 Microhardness Measurement

Hardness studies have been carried out on BTCA using Vicker's microhardness tester. The selected surface of crystal was polished using a velvet cloth to get a smooth surface. Microhardness measurements were taken for various applied loads of 25, 50 and 100 g and keeping the time of indentation constant at 10 s for all the cases. A graph plotted between hardness value (H_v) and applied load is shown in Figure 8. From the plot it is inferred that the hardness value of the complex decreases with increase in the applied loads. An increasing trend is observed in the hardness values with increasing applied loads and hence the indentation size effect (ISE) is satisfied with increasing loads. The value of hardness was calculated using the equation, $H_v = 1.8544 P/d^2 \text{ kg mm}^{-2}$. According to Mayer's law, $P = ad^n$. The plot between $\log d$ and $\log P$ is shown in Figure 9. The value of work hardening co-efficient, n was calculated from the slope of the straight line. The value of ' n ' for this complex was found to be 1.4. From the value of ' n ' (less than 1.6) it is inferred that the complex, DAPP is a hard material.

3.8 Dielectric Studies

The variation of dielectric constant and dielectric loss were carried out as a function of applied frequency from 50 Hz to 5 MHz at room temperature. The opposite parallel faces of the crystals were coated high-grade silver paste placed between two copper electrodes and thus parallel plate capacitor was formed. The capacitance and dielectric loss were measured for different frequencies from 50 Hz to 5 MHz. The dielectric constant (ϵ_r) of the complex was calculated using the equation, $\epsilon_r = C_t / \epsilon_0 A$, where C_t is the capacitance, d is the thickness of the crystal, ϵ_0 is the vacuum dielectric constant and A is the area of the crystal. The variation of dielectric constant as a function of $\log \nu$ is shown in Figure 10. The values of dielectric constant decrease with increase in frequency. At lower frequency region the values of dielectric constant are high and at high frequency region the values of dielectric constant are low. The variation of dielectric loss with $\log \nu$ is shown in Figure 11. From the plot, it is observed that the values of dielectric loss decrease with increase in frequency. It has low value in the higher frequency region. The low dielectric loss with high frequencies for the complex indicates that the material possesses enhanced optical quality with lesser defects and hence the complex can be used as an NLO material.

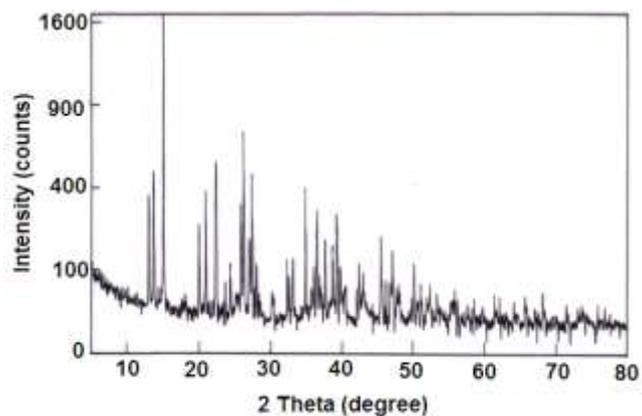


Figure 2. Powder XRD pattern of BTCA crystal

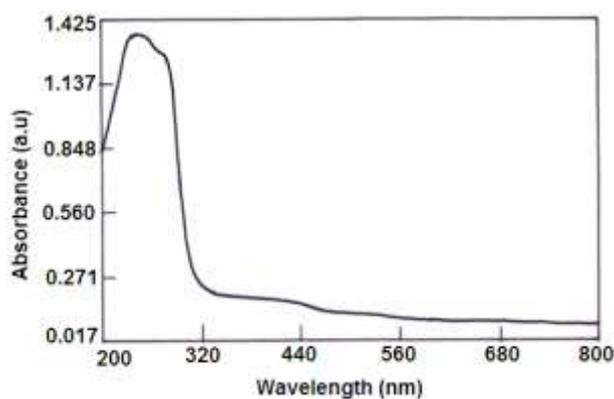


Figure3. UV-visible spectrum of BTCA crystal

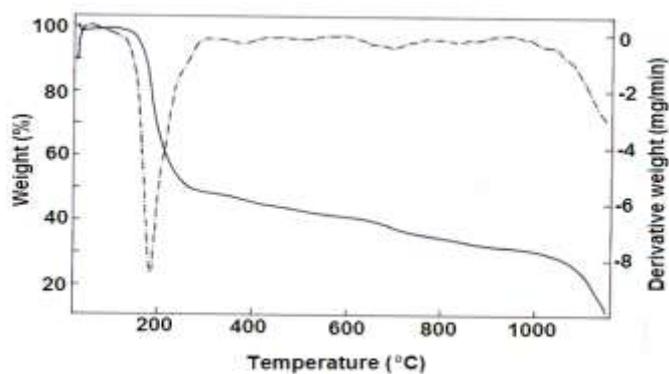


Figure4. TG-DTG thermogram of BTCA crystal

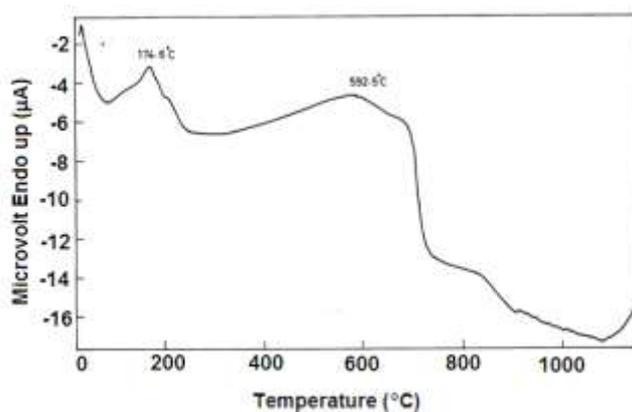


Figure 5. DTA thermogram of BTCA crystal

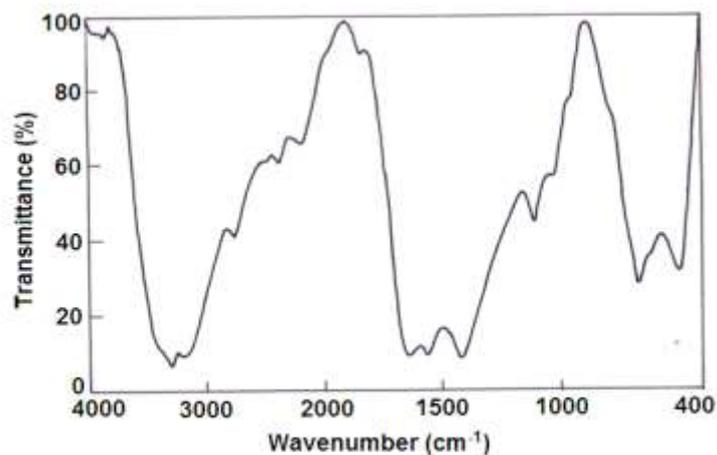


Figure6. FTIR spectrum of BTCA crystal

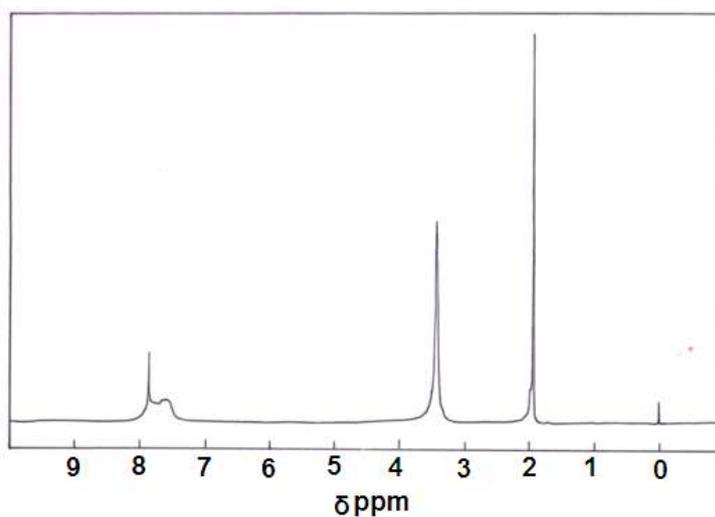


Figure 7. ¹H MNR spectrum of BTCA crystal

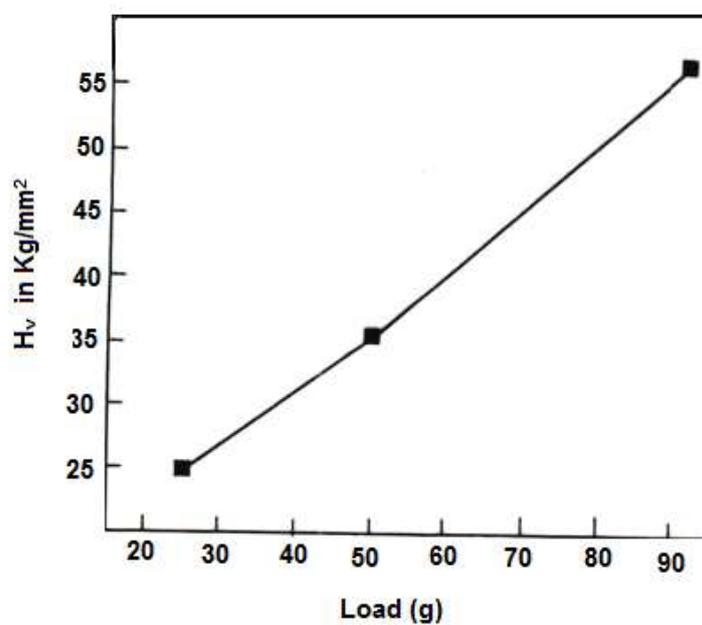


Figure 8. Variation of hardness with applied load of DAPP complex

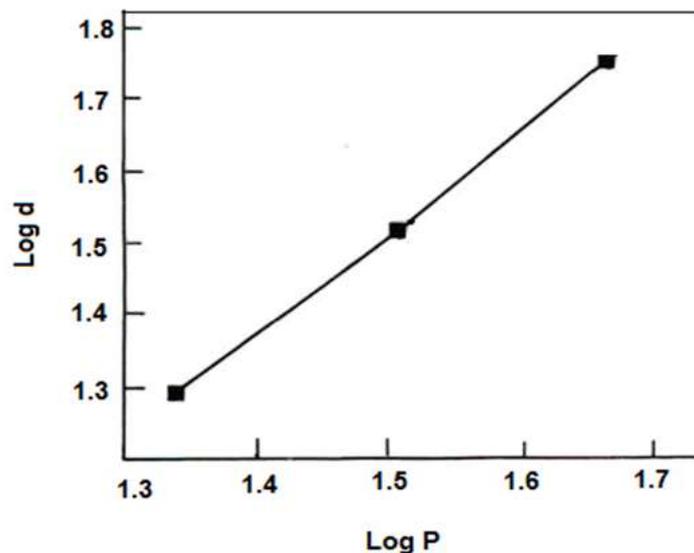


Figure 9. Plot of log d versus log P of DAPP complex

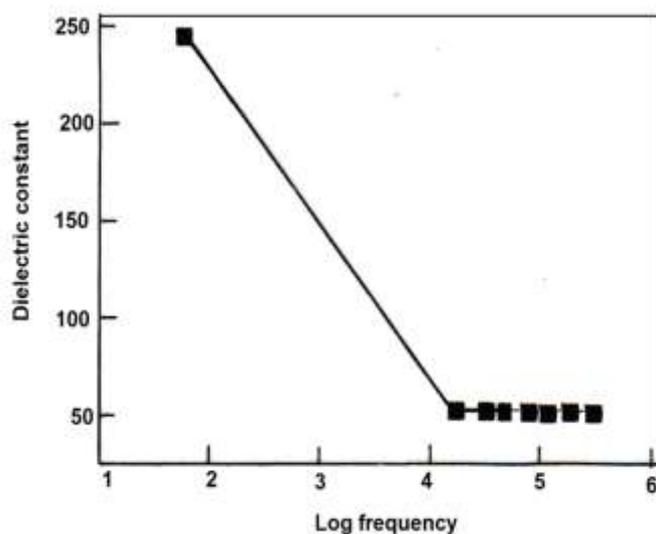


Figure 10. Variation of dielectric constant with log frequency

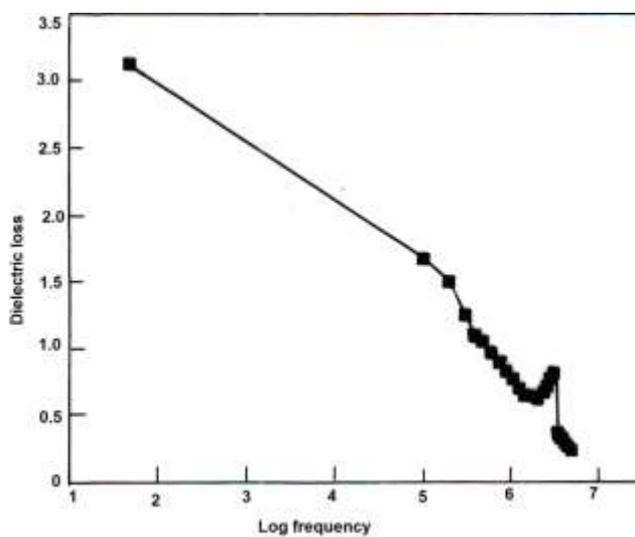


Figure 11. Variation of dielectric loss with log frequency

IV. Conclusions

- ❖ Single crystal of bisthiourea calciumacetate was grown from saturated solution by slow evaporation solution growth technique at room temperature.
- ❖ The elemental analysis data of compound confirms stoichiometric ratio of the compound.
- ❖ The crystalline nature of the compound was confirmed by the sharp and well defined Bragg peaks obtained in the powder X-ray diffraction pattern.
- ❖ The optical property of the compound was confirmed by UV-visible absorption study.
- ❖ The thermal stability and decomposition pattern of the compound were studied using TG-DTA studies.
- ❖ The characteristic absorption bands due to various chemical bonds were assigned through FTIR spectroscopic techniques.
- ❖ The proton environment of the compound was confirmed by the NMR spectral study.
- ❖ The SHG efficiency of the compound indicates that the compound has SHG efficiency.

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