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Synthesis, XRD, spectral and thermal studies of semi-organic non-linear optical material: 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 molecular formula 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 number of protons environment of the compound was confirmed by the NMR spectral studies. The thermal stability and decomposition pattern of the compound were formulated using TG-DTA studies. The heating and cooling cycles observed in DSC analysis 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 SHG efficiency of the compound indicates that the compound has SHG efficiency twice than that of standard KDP.

Keywords: Crystal, FTIR, XRD, TG-DTA, NMR

1. INTRODUCTION

Organic molecules with significant nonlinear optical activity generally consist of a π-electron conjugated moiety substituted by an electron donor group on one end of the conjugated structure and an electron acceptor group on the other end forming a “pushpull” conjugated. The donor and acceptor groups provide the ground state charge asymmetry of the molecule, which is required condition for second order nonlinearity [1]. Crystalline organic charge transfer complex have a vital role in biological systems such as antimicrobial activity and DNA-binding, in addition to in laser technology, optoelectronics, optical communications, photo catalysis and optical signal processing [2-9]. Organic derivatives are also used in human therapy such as treatment of burns, antiseptic and astringent agents [10]. Organic complexes play a central role in bioelectrical and biological systems such as bactericides, fungicides, insecticides and various light-driven physical and chemical processes [11-14]. In general, organic nonlinear optical materials are found to have high nonlinear coefficient equated to those of inorganic materials [16,17].

On the basis of these facts, in this present work, we describe the synthesis and characterization of bisthiourea calciumacetate crystal (hereafter abbreviated as BTCA). Characterization of the grown crystals was made using NMR spectroscopic techniques. The FTIR spectroscopic technique was used to find out the various characteristic absorption bands present in the compound.

2. EXPERIMENTAL DETAILS

2.1. Materials

Analytical grades of chemicals were obtained from Sigma-Aldrich and used without further purification. The solvent methanol used is High Pressure Liquid Chromatography (HPLC) grade.

2.2. Characterization techniques

The solubility study of the complex was analyzed at different temperature between 30 and 60°C with increments of 5°C using constant temperature bath Ragaa instrument model. The NMR spectra of the complex were carried out using a Bruker DRX 400MHz model spectrometer using $Si(CH_3)_4$ [TMS] as the internal standard and d 6-DMSO as the solvent. The mechanical property of the complex was measured using Vicker’s microhardness test.

3. 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, Nitrogen and Sulphur 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 data of BTCA crystal

	Carbon %	Hydrogen %	Nitrogen %	Sulphur %
Experimental	19	3.15	14.73	18.15
Calculated	23.20	4.52	18	20.62

3.2. Powder X-ray diffraction method

The powder X-ray diffraction pattern of BTCA is shown in figure 1. The sharp and well defined Bragg peak at specific 2θ value in the powder XRD pattern confirms its crystallinity.

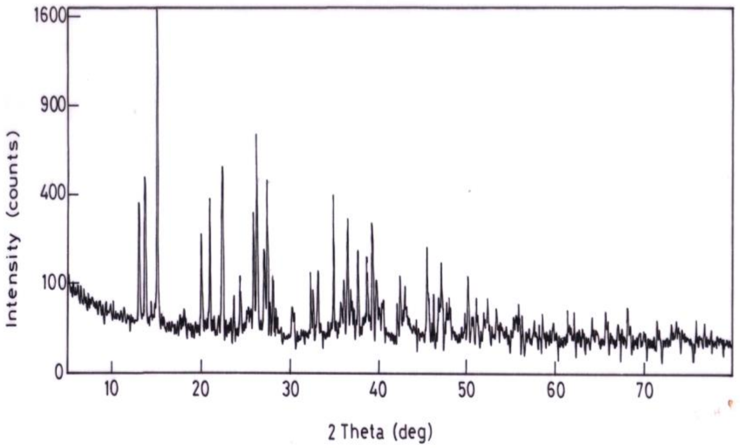

Figure 1 Powder XRD pattern of BTCA crystal

3.3. UV- visible absorption spectral studies

The UV- visible spectrum of BTCA is shown in figure 2. The UV visible spectrum gives limited about the structure of UV and visible light involves promotion of the electron in the σ and π orbital from the ground state to higher energy state. The compound shows absorption at 235 nm and there is no remarkable absorption in the entire visible region of the spectrum. The absorption maximum at 235 nm is to be assigned to n-π^* transition of constituent group. The absence of absorption between 235 and 800 nm shows that the compound useful for second harmonic generator optoelectronic application.

3.4. Nuclear magnetic resonance (NMR) spectroscopy

3.4.1. The H^1 spectrum

The appearance of two distinct signals in the spectrum indicates two different protons NMR the signal at 83.4 ppm is assigned to CH_3 protons. The N-H proton signal appears between 87.5 to 8.4 ppm. The signal 1.94 ppm is assigned to solvent peak. The TMS signal appears at 0 ppm.

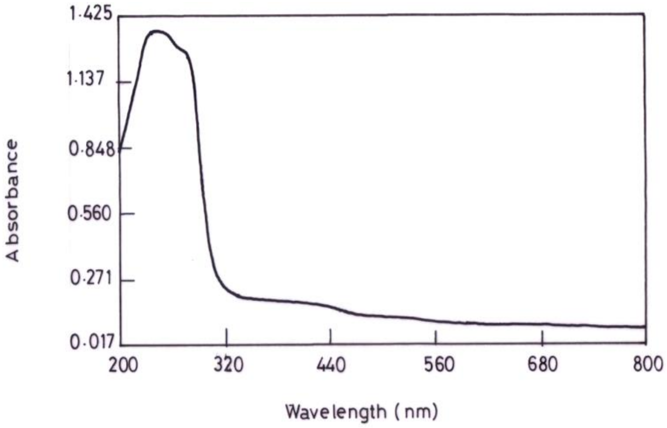

Figure 2 UV-visible spectrum of BTCA crystal

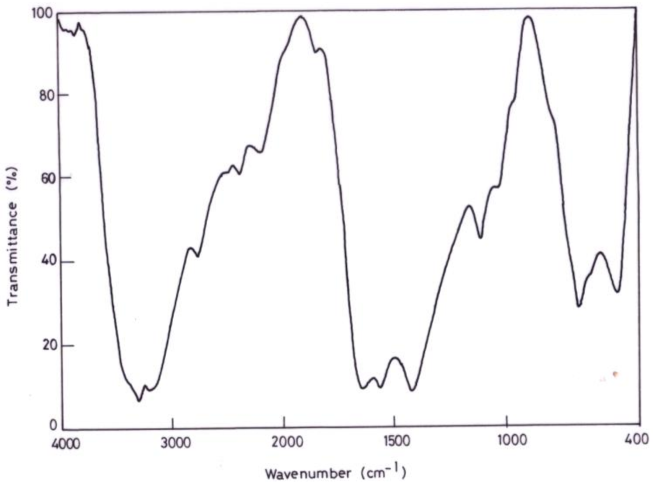

Figure 3 NMR-spectrum of BTCA crystal

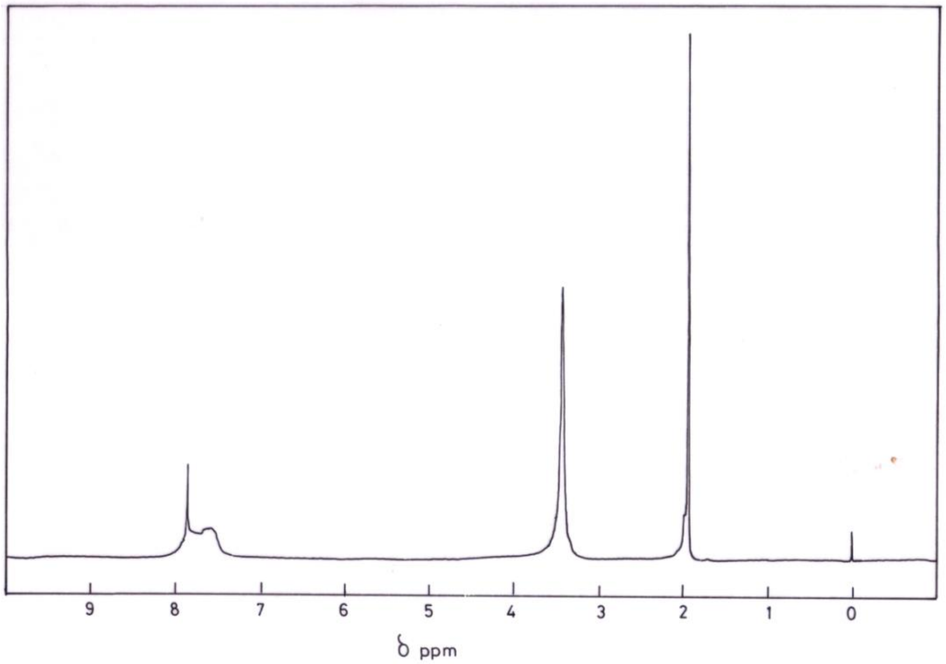

Figure 4 FTIR- spectrum of BTCA crystal

3.5. FTIR spectrum

The absorption frequencies and their assignments are given in table 2. The NH_2 stretching vibration is absorbed at 3285 cm^{-1}. The absorption at 3193 cm^{-1} is assigned to N-H stretching vibration. The C-H stretching vibration is absorbed at 2751 cm^{-1}. The absorption at 2381cm^{-1} is characteristic of C-C bond stretching vibration. The combination band and overtone for appear at 2184cm^{-1}. The NH_2 bending vibration absorbed 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 absorbed 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.

Table 2 FTIR-spectral data of BTCA crystal

Wavenumber in cm^{-1}	Assignment
3285	NH_2 stretching vibration
3193	N-H stretching vibration
2757	C-H stretching vibration
2381	C-C bond stretching vibration
2184	combination band and overtone
1880	NH_2 bending vibration
1632	N-H bending vibration
1559	stretching vibration of COO^- group
1414	C-N stretching vibration
1106	N-H rocking vibration
663 & 488	C=S stretching vibration and N=C=N bending vibration

3.6. Thermal analysis

3.6.1. Thermogravimetric analysis

The The TG-DTG thermograms of the compound BTCA are shown in Figure 5. 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.

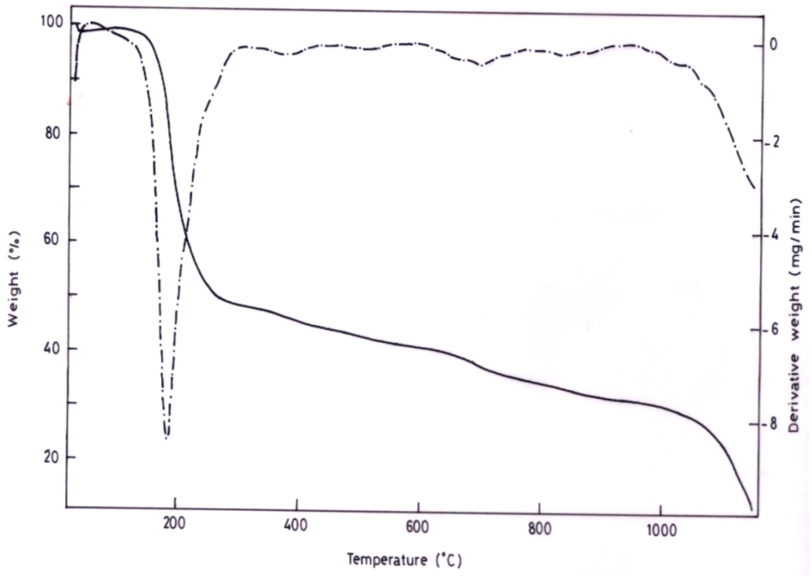

Figure 5 TG curve of BTCA crystal

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.

3.7. Differential thermal analysis

The DTA curve of the compound BTCA is shown in Figure 6 Two endothermic peaks are observed. The endothermic peaks appear between 170 and 700°C is due to the decomposition of the compound.

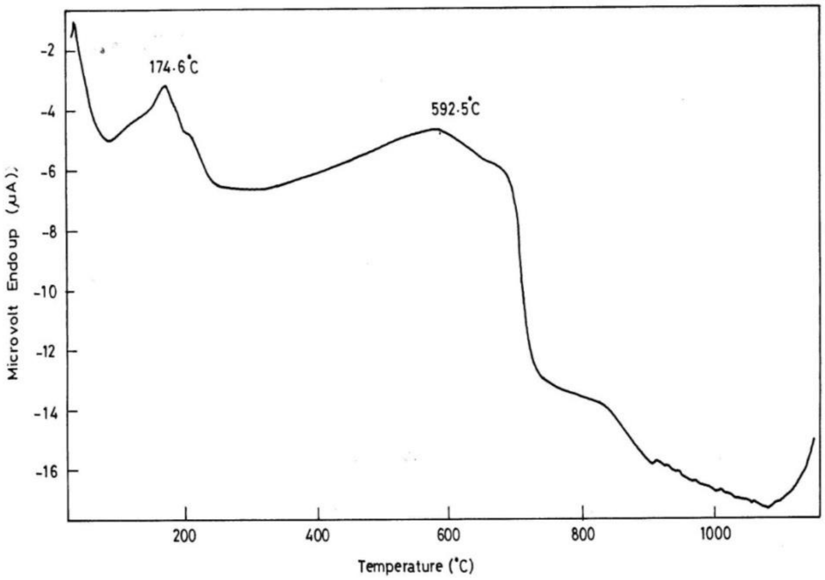

Figure 6 DTA curve of BTCA crystal

3.8. Differential scanning calorimetry

The low temperature DSC curve of crystal is shown in Figure 7. They are two thermal anomalies observed in the heating and cooling cycles. The cooling cycle shows a thermal anomaly at the peak temperature -31.93°C and in the heating cycle at the peak temperature 1.09°C. The compound shows thermal hysteresis during the heating and cooling cycles.

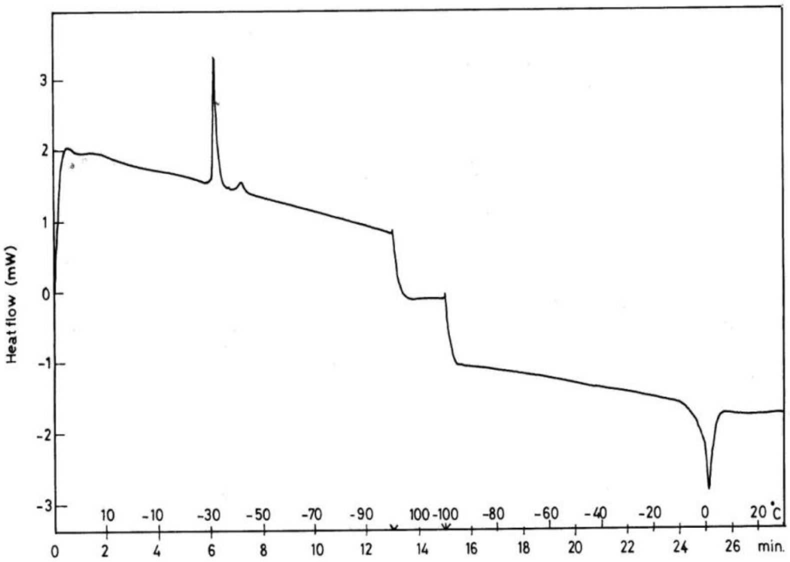

Figure 7 DSC Cooling and Heating curves of BTCA crystal

4. 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 the molecular formula 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 proton environment of the compound was confirmed by the NMR spectral studies. The thermal stability and decomposition pattern of the compound were studied using TG-DTA studies. The heating and cooling cycles observed in DSC analysis indicates that the compound shows first order phase transition. The characteristic absorption bands due to various chemical bonds were assigned through FTIR spectroscopic techniques. The SHG efficiency of the compound indicates that the compound has SHG efficiency twice than that of standard KDP.

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