Research Article

Synthesis, Spectral, Thermal and Optical Studies on Semiorganic Nonlinear Optical Material: Ditetraethylammonium Tetrabromocuprate(II) Dihydrate

T. Dhanabal[1], G. Amirthaganesan[2]*, M. Dhandapani[2]

[1]Department of Chemistry, Muthayammal College of Engineering, Namakkal-637 408, Tamil Nadu, India.
[2]Department of Chemistry, Ramakrishna Mission Vidyalaya College of Arts and Science, Coimbatore-641 020, Tamil Nadu, India.

Abstract

Single crystals of ditetraethylammonium tetrabromo cuprate(II) dihydrate were grown by slow evaporation solution growth method at room temperature. The C H N analysis was studied to confirm the stoichiometry of the synthesized compound. The sharp and well defined Bragg peaks observed in the powder X-ray diffraction (XRD) pattern confirm the crystalline nature of the compound. The unit cell parameters of the compounds was measured and observed that the grown compound crystallized in monoclinic crystal system. The thermal stability and decomposition pattern of the compound were studied by thermogravimetry-differential thermal gravimetry and differential thermal (TG-DTG and DTA) analyses. The FTIR spectrum characterizes the various chemical bonding and water molecules in the compound. The nonlinear optical property of the material was analyzed by modified Kurtz-Perry powder technique.

***Corresponding Author**
E-mail: profga@yahoo.co.in;
Fax: +91 422 2693812;
Tel: +91 9442002233.

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Introduction

Materials with excellent nonlinearities have been studied extensively for their possible applications in various fields like telecommunication, optical computing, optical data storage and optical information processing [1,2]. Most of the organic NLO crystals are constituted by weak van der Waals and hydrogen bonds. So they are soft in nature and it is difficult to cut and polish the crystal due to its softness [3]. The mechanical strength of organic crystal is very low. Pure inorganic NLO materials typically have excellent mechanical and thermal properties but possess relatively modest optical nonlinearities because of the lack of extended π-electron delocalization. Their benefits are the combination of desirable properties of inorganic materials, such as, a wide range of electronic characteristics, mechanical hardness and thermal stability and on the other hand, structural variety, large polarizability and easy processing of the organic molecules [4]. For further enhancement of NLO property many efforts have been made on developing new semiorganic NLO materials. Pure inorganic NLO materials typically have excellent mechanical and thermal properties but possess relatively modest optical nonlinearities because of the lack of extended π-electron delocalization. To overcome these problems, the research of combination of organic and inorganic hybrid compounds leads to find a new class of materials for electronic industries, called semi-organic materials [5]. The complex of organic–inorganic gives semi-organic material, which possesses higher mechanical strength compared to organic materials [6].

Based on the above facts we reported the synthesis and characterization of new nonlinear optical material, ditetraethylammonium tetrabromocuprate(II) dihydrate (hereafter abbreviated as TEATB-Cu). The grown crystals were characterized by elemental analysis, power X-ray diffraction, thermal, spectral and optical studies.

Experimental

Materials and method

TEATB-Cu was synthesized by sow evaporation solution growth method tetraethylammoniumbromide and copper(II) bromide (AR grades), taken in 2:1 molar ratio. Calculated amounts of the materials were weighed and transferred into a beaker, dissolved in double distilled water and stirred well for about 2 h with the help of a temperature controlled motorized magnetic stirrer to make a homogeneous solution of the material for proper chemical reaction. Then the solution was allowed to evaporate at room temperature. The TEATB-Cu crystals were obtained as per following equation 1.

$$2[N(C_2H_5)_4]Br + CuBr_2 + 2H_2O \xrightarrow[\text{(Solvent)}]{} [N(C_2H_5)_4]_2CuBr_4.\,2H_2O \quad \text{(TEATB-Cu)}$$

Bright, transparent and colourless TEATB-Cu crystals were obtained under the experimental conditions. The crystal took place within 20 to 25 days with average dimensions up to 1.2×0.4×0.2 cm3. 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 TEATB-Cu crystal is shown in Figure 1.

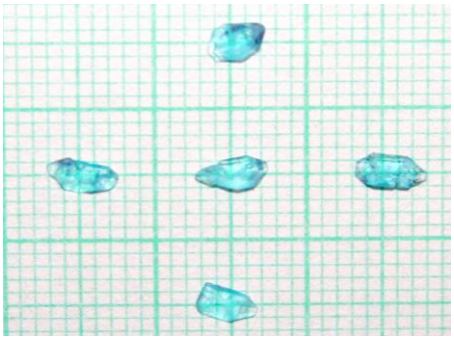

Figure 1. Photograph of TEATB-Cu crystal

Characterization

A VARIO ELIII model analyzer was used to analyze C, N and H in the crystal. The powder XRD pattern of TEATB-Cu crystal was obtained using BRUKER AXS D8 Advance X-ray diffractometer model instrument with Cu Kα radiation (λ = 1.54060 Å) at room temperature. Enraf Nonius CAD4-MV31 Bruker Kappa APEXII instrument was used to determination of unit cell parameters of the crystal. The thermal analyses (TG-DTG and DTA) of TEATB-Cu were recorded using a PERKIN ELMER DIAMOND thermal analyzer under nitrogen atmosphere. The samples were heated from room temperature to 850ºC at a heating rate of 10ºC per minute. The FTIR spectra of the crystal were recorded using a PERKIN ELMER Model RX1 instrument. The SHG efficiency of the complex was studied by modified Kurtz-Perry powder technique using Nd:YAG laser.

Results and discussion

Elemental analysis

The elemental analysis shows that the compound contains C: 27.64% (29.82%), H: 5.18% (6.21%) and N: 2.94 % (4.34%). The results indicate that both experimental and theoretical values (given in brackets).The experimental values of carbon, hydrogen and nitrogen are very close to the calculated values. Thus the stoichiometry of the compound is confirmed.

Powder X-Ray Diffraction Method

The powder X-ray diffraction pattern of the TEATB-Cu crystals is shown in Figure 2. The sharp and well defined Bragg peaks in the powder XRD pattern confirm the crystalline nature of the compound.

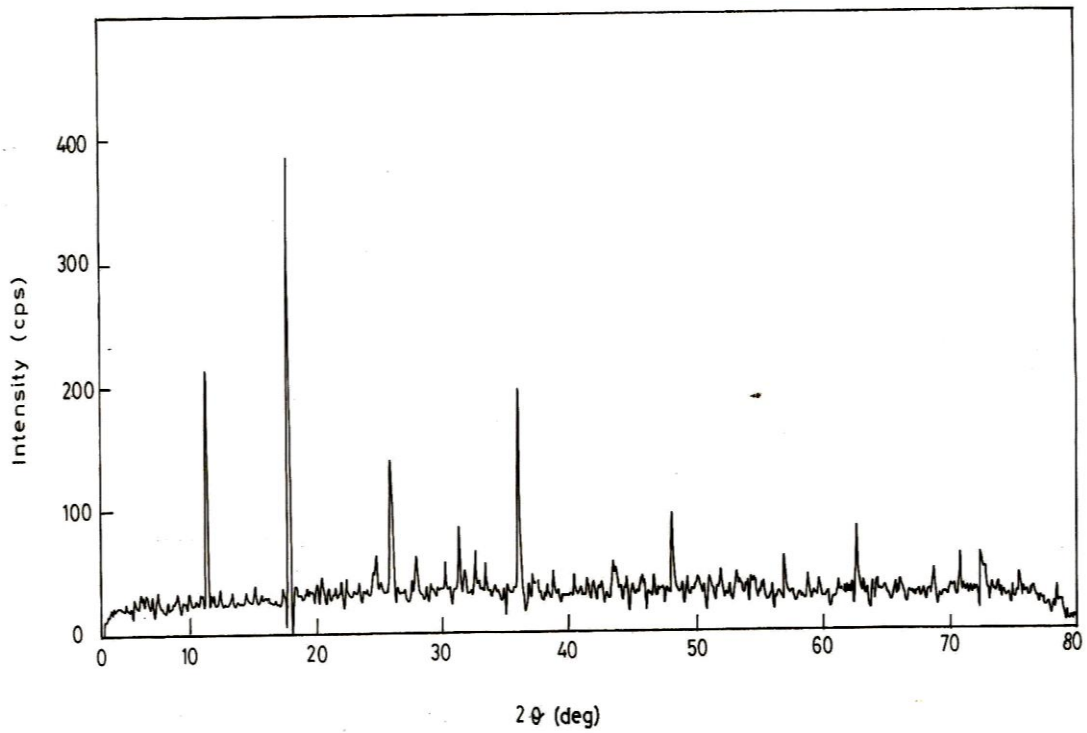

Figure 2. Powder X-ray diffraction pattern of TEATB-Cu crystal

Determination of Unit Cell Parameters

The unit cell parameter for TEATB-Cu crystal is found to be a = 6.15 Å, b = 12.09 Å, c = 9.07 Å and α = 90.00˚ , β = 104.46˚, γ = 90.00˚, V = 653 Å3. This indicates the compound crystallizes in monoclinic crystal system.

Thermal Analyses

Thermogravimetry-Differential Thermal Gravimetry Analysis (TG-DTG)

The TGA of TEATB-Cu crystal is shown in the Figure 3. The compound is subjected to a uniform heating at a rate of 10°C per minute under nitrogen atmosphere. The weight loss occurs in two steps as shown in the thermogram. The possible decomposition pattern for the compound is formulated as follows,

Step I 90°C - 360°C

$[N(C_2H_5)_4]_2CuBr_4.2H_2O \longrightarrow 2H_2O\uparrow + N_2 \uparrow + 2C_2H_5Br \uparrow + C_{12}H_{30} \uparrow + CuBr_2$

Molecular weight = 697.5

Step II

Above 500°C

$CuBr_2 \longrightarrow$ Vapourises or decompose

Step I

In the first step the compound, TEATB-Cu on heating is stable up to 90°C and then it decomposes to eliminate two molecules of water, a molecules of nitrogen and two molecules of ethyl bromide and some hydrocarbon moiety of molecular formula C12H30. This is explained in the above equation. This occurs between 90 and 360°C. The experimental weight loss is 58%. The calculated weight loss based on the decomposition pattern described above

accounts for 67.1%. The difference in weight losses is 9.1% which is due to the adsorbed moisture. Copper compounds are usually associated with water of hydration and adsorbed moisture.

Step II

Copper bromide formed is somewhat stable up to 500°C and it starts decomposing above 500°C. The thermogram shows a sudden weight loss above 670°C. Thus TGA study confirms the presence of two molecules of water of crystallization and adsorbed moisture. The stoichiometry of the compound is also verified by the TGA study. The derivative curve (DTG) confirms weight losses observed in the TGA curve.

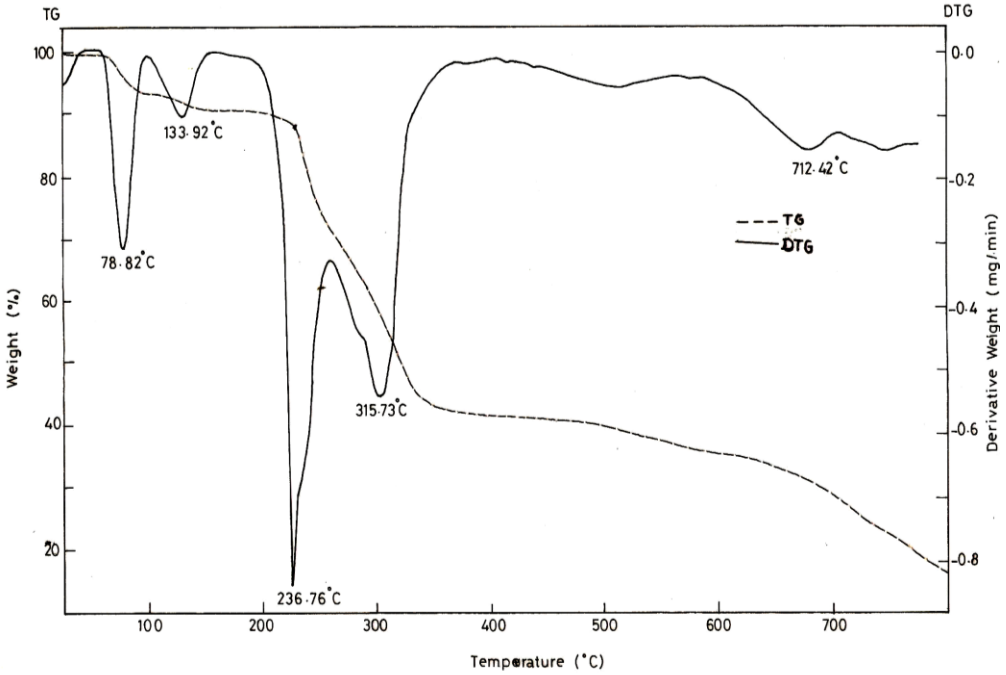

Figure 3 TGA – DTG curves of TEATB-Cu crystal

Differential Thermal Analysis (DTA)

The DTA thermogram of TEATB-Cu crystal is shown in Figure 4. The endothermic peaks indicate the decomposition of the compound occurring between 90 and 340°C. The two long endothermic peaks with peak temperatures 83.04°C and 241.28°C must involve some phase transition. The enthalpy change and their values at various stage of decomposition are shown in Table 2.

Table 1. Enthalpy values of TEATB-Cu Crystal

S.No.	Peak temperature (°C)	Enthalpy (kJ/mol)
1	83.04	117.527
2	138.15	48.978
3	220.17	9.740
4	241.28	112.724
5	324.51	62.260

FTIR Spectral Studies

FTIR spectrum of TEATB-Cu crystals is shown in Figure 5. The absorption band observed at 3393cm-1 is due to the O-H stretching vibrations. A sharp peak at 2973 cm-1, and 2944 cm-1 are due to the C-H symmetric stretching and asymmetric stretching vibration of ethyl group respectively [7]. C-H deformation mode of vibration occurs at 1456 cm-1 [8]. The C-N stretching vibration is observed at 1308 cm-1 and 1032 cm-1. A sharp peak at 785 cm-1 is due to C-H rocking. The skeletal vibration of CuBr42- ions occurs at 617 cm-1 and 467 cm-1.

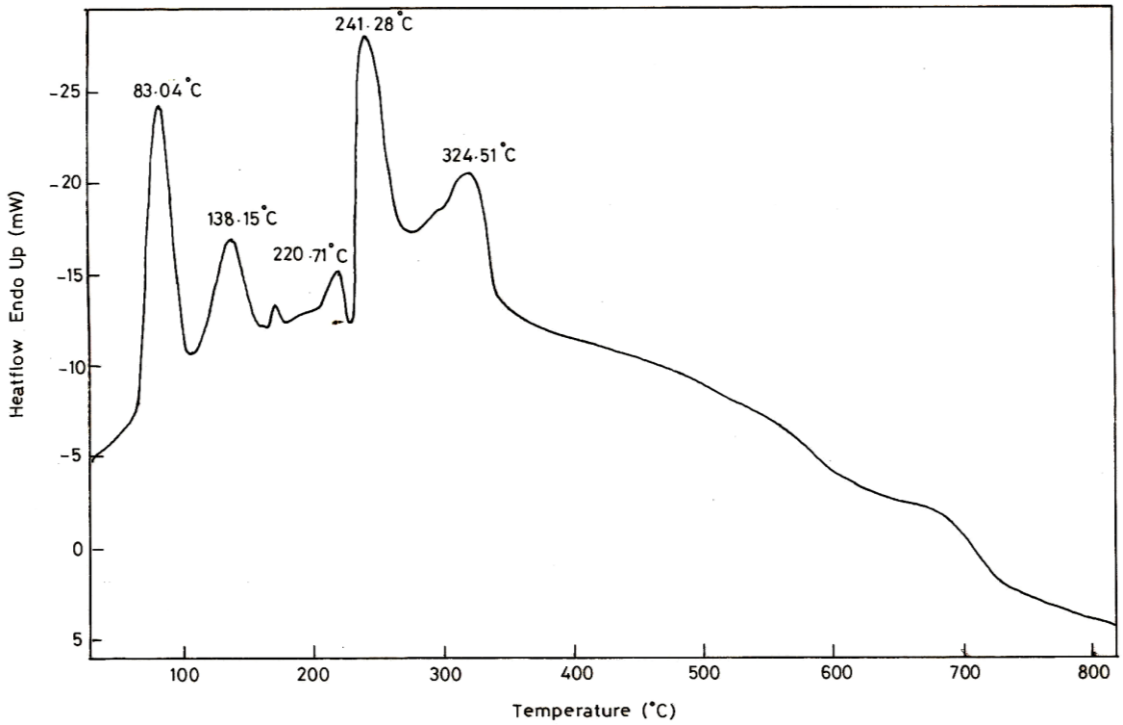

Figure 4 DTA thermogram of TEATB-Cu crystal

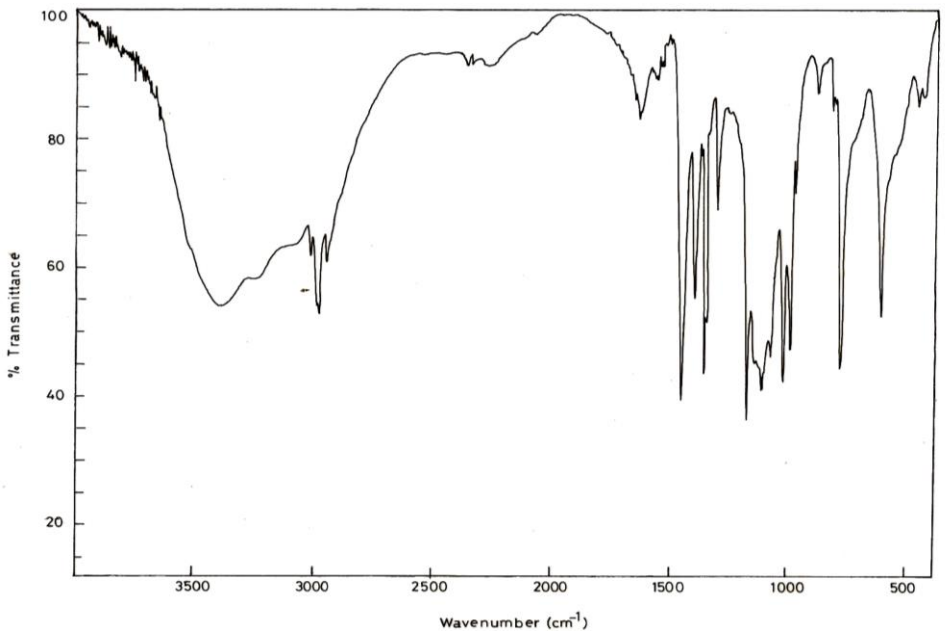

Figure 5. FTIR spectrum of TEATB-Cu crystal

Nonlinear Optical (NLO) Property

The second harmonic generation efficiency was determined by the modified version of the powder technique developed by Kurtz and Perry [8] using a Nd:YAG laser with a pulse repetition rate of 10 Hz working at 1064 nm. Crystals of TEATB-Cu were powered with a uniform particle size and then tightly packed in a microcapillary 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 from Q-switched laser was focussed onto the crystals. and exposed to laser radiation. Second harmonic

radiation generated by the randomly oriented microcrystals was focused by a lens and detected by a photomultiplier tube. A sample of KDP was used as a reference material. SHG conversion efficiency was computed by the ratio of signal amplitude of TEATB-Cu sample to that of the KDP signal amplitude recorded for the same input powder. The SHG efficiency of KDP and the compound has been measured as 24 mV and 5 mV, respectively. It is observed that the SHG efficiency of the grown TEATB-Cu compound was found to be twice than that of KDP. The SHG efficiency of the synthesized compound may be due to the effect of intermolecular hydrogen bonding between the tetraethylammoniumbromide and copper (II) bromide in the compound will enhance the hyperpolarizability (β) value, which is the required property for a system to exhibit a nonlinear optical process. As a result the grown material can be used as a NLO material.

Conclusions

Single crystals of ditetraethylammonium tetrabromocuprate(II) dihydrate were prepared and crystallized by slow evaporation solution growth method at ambient temperature. The stoichiometric ratio of the compound was confirmed by elemental analysis. The crystalline nature of the compound was confirmed by powder X-ray diffraction method. The unit cell parameters of the compound were calculated and indicate that the synthesized compound belongs to monoclinic crystal system. The TG-DTG and DTA analyses were used to find out the thermal stability and decomposition pattern of the title compound. The characteristic vibration bands and water molecules present in the compound were observed in the FTIR spectroscopic technique. The SHG efficiency of the compound shows that the compound has SHG efficiency twice than that of standard, KDP.

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