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# Synthesis, spectral and thermal characterization of Bis(diethylammonium) tetrachloromercurate(II)-An nonlinear optical material

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ABSTRACT

A new semiorganic compound, bis(diethylammonium) tetrachloromercurate(II) was grown by slow evaporation solution growth technique at ambient temperature from its aqueous solution. The crystal system and the cell parameters have been identified from the powder X-ray diffraction pattern. The UV–visible absorption of the compound shows absorption at 246 nm and there is absorption observed in the entire visible region indicates that the compound can be used as a nonlinear optical material. The UV–visible transmittance spectrum of grown crystal shows a lower cut-off wavelength at 275 nm and it was found that the crystal is suitable for optoelectronic applications. Thermal studies were carried out to find out the thermal stability and confirm the stoichiometric ratio of the compound. The thermal anomalies in DSC study indicate the occurrence of first order transition in the compound at low temperatures. The FTIR spectrum of the compound characterizes various functional groups. The various kinds of protons and carbons were assigned through NMR ($^{1}$H and $^{13}$C) spectroscopic techniques. The SHG efficiency of the compound was studied by Kurtz-Perry power technique and observed that it has SHG efficiency 1.5 times greater than that of potassium dihydrogen phosphate (KDP). The dielectric constant and dielectric loss of the compound decreases with increase in frequency.



## 1. Introduction

In the recent years, extreme efforts have been made to develop new inorganic, organic and semi organic nonlinear optical (NLO) materials [1–6]. The NLO materials in their single crystal form exhibiting large optical nonlinearity are also of great interest for telecommunication, optical information processing and high optical disc data storage [7–9]. Hence, there is a great demand to synthesize new NLO materials and grow their single crystals. Organic crystals are having some special properties of large optical nonlinearity and low cut-off wavelengths in UV region, therefore the organic NLO crystals are required for use in optical devices. Organic materials are often formed by weak van der Waals forces and hydrogen bonds and hence possess a high degree of delocalization. However, these organic crystals have certain limitations such as poor mechanical and thermal stability. 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 [10]. The complex of organic–inorganic gives semi-organic material, which possesses higher mechanical strength compared to organic materials [11]. Based on the above fact in the present investigation, we have reported a new semi-organic nonlinear optical bis(diethylammonium) tetrachloromercurate(II) (hereafter abbreviated as BDAC-Hg). The grown crystals were subjected to various physical characterizations to ascertain the formation of the compound and understand its properties. Spectroscopic techniques such as UV–visible absorption, optical transmittance study, FTIR spectrum, powder X-ray diffraction, thermal studies (TG-DTA and DSC), nonlinear optical property and dielectric studies have also been undertaken and reported.

## 2. Experimental details

### 2.1. Material synthesis

The compound was synthesized and grown by slow evaporation solution growth method at room temperature from its aqueous solution. Diethylammonium chloride (E-Merck, Germany) and mercuric chloride (analytical grade) were dissolved separately in triply distilled water in 2:1 ratio, respectively. The two solutions were mixed and stirred well for about 1 h using magnetic stirrer to

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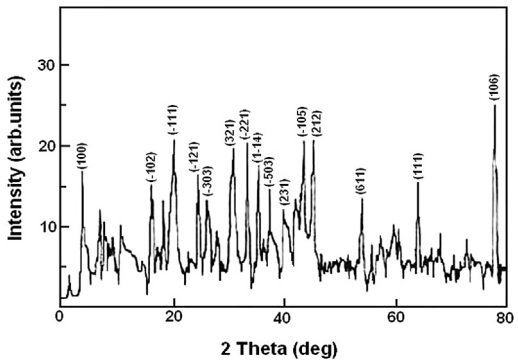


**Fig. 1.** Powder X-ray diffraction pattern of BDAC-Hg crystal.

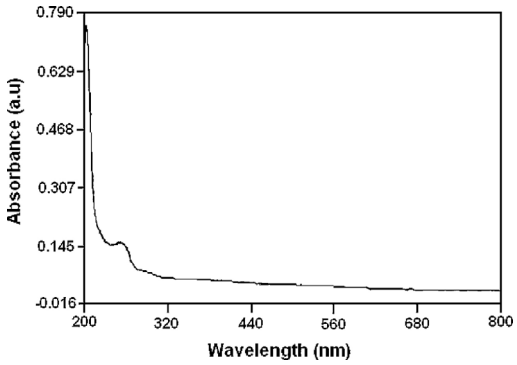


**Fig. 2.** UV–visible spectrum of BDAC-HG crystal.

ensure homogeneity. The thoroughly mixed solution was filtered and transferred to crystal growth vessel and covered with a perforated sheet to facilitate the evaporation of the solvent at ambient temperature. Single crystals with perfect shape were obtained by spontaneous nucleation. Care was taken to minimize temperature gradient and mechanical shake during the crystal growth period. The crystals were formed as per the following equation

$$2[NH_2(C_2H_5)_2Cl] + HgCl_2 \overset{\text{Medium } H_2O}{\longrightarrow} [NH_2(C_2H_5)_2]_2HgCl_4$$

The crude material was subjected to repeated recrystallization till ultra pure crystals were obtained. The bright, transparent, needle-shaped and colourless crystals were obtained within a period of 20 days under the experimental conditions.

### 2.2. Characterization techniques

The powder XRD pattern of compound was obtained using Bruker AXS D8 Advance X-ray diffractormeter with Cu Kα radiation (λ = 1.54060 Å) at room temperature and the sample was scanned over the range of 0–80° at a scan rate of 1/min. The absorption and optical transmission spectra of the crystal were measured using JASBO V-550 UV–Vis–NIR spectrophotometer in the range 200–800 nm. The TG-DTA analysis was carried out using a Perkin Elmer Diamond thermal analyzer under nitrogen atmosphere. The low temperature DSC study of the compound was obtained using a NETZSCH DSC 204 instrument under nitrogen atmosphere at a heating rate of 10 K/min. The sample was cooled from room temperature to −100 °C and heated back to room temperature. The FTIR spectrum of the compound was recorded in a Perkin Elmer Model RX1 model instrument using KBr pellet technique at room temperature. The NMR spectrum of BDAC-Hg crystal was carried out using Bruker AVIII 500 MHz NMR instrument model. The SHG efficiency of the complex was studied by modified Kurtz-Perry powder technique using Nd:YAG laser. The dielectric properties were studied at room temperature using TH 2816A Digital LCRZ Meter in the frequency region 50 Hz–2 MHz.

## 3. Results and discussion

### 3.1. Powder X-ray diffraction method

The powder X-ray diffraction pattern of the crystal with the peak indexations is shown in Fig. 1. The sharp and well defined Bragg peaks in the powder X-ray diffraction pattern confirm the crystalline nature of the compound. The prominent peaks in the powder pattern have been indexed using CRYSFIRE software programme. The unit cell parameters are found to be a = 13.0088 Å, b = 7.8941 Å, c = 10.8851 Å and $\alpha = \gamma = 90°$, $\beta \neq 90°$. The unit cell volume is 1002.54 Å$^3$. From the unit cell parameters it is observed that the crystal belongs to monoclinic system with space group $P2_1/n$.

### 3.2. UV–visible absorption spectral study

The optical transmission spectrum of the crystal is shown in Fig. 2. From the spectrum it is seen that the crystal shows absorption at 249 nm and there is no remarkable absorption in the entire visible region of the spectrum. The absorption at 249 nm is assigned to n-σ* transition in diethylammonium moiety. The absence of absorption in the region between 250 and 800 nm shows that the crystal is a useful candidate for the optoelectronic applications.

### 3.3. UV–visible transmittance study

The UV–visible transmittance spectrum of the compound is shown in Fig. 3. The compound shows a lower cut-off wavelength at 248 nm. The cut-off wavelength at 248 nm in the compound is due to the n-σ* transition in diethylammonium moiety. The transmittance between 249 and 800 nm is approximately 90%. The crystal has sufficient transmission in the visible region. The absence of absorption in the region from 249 to 800 nm indicates that the compound suitable for optoelectronic application.

### 3.4. Thermal analyses

#### 3.4.1. Thermogravimetry

The TG thermogram (dotted curve) of the crystal is shown in Fig. 4. The compound was heated from room temperature to 320 °C at a heating rate of 10 °C/min under nitrogen atmosphere. The compound decomposed completely between 210 and 320 °C. The following decomposition pattern has been formulated to

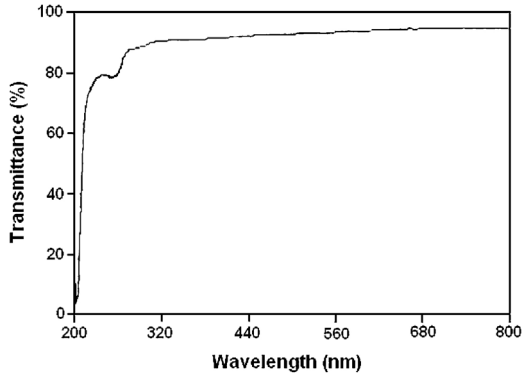


**Fig. 3.** Optical transmittance spectrum of BDAC-Hg crystal.