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# Observation of crystallization and characterizations on thiourea cadmium iodide: A semi-organic optical material

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ABSTRACT

In this work, the single crystals of thiourea cadmium iodide were grown by slow evaporation solution technique in two different ratios 2:1 and 1:1. During the formation of their single crystals the morphological features and its live growth process were recorded with the help of inverted microscope. Structural studies of the grown crystals have been carried out by powder X-ray diffraction to confirm the crystal system and vibrational modes by Raman spectroscopy. The optical energy band gaps were investigated through UV–vis spectroscopy study. The surface morphology of the grown single crystals was analyzed by using Scanning Electron Microscope and thermal analysis was carried out by using thermogravimetric analysis. The electrical properties were also studied as a function of frequency and the obtained results are discussed.



## 1. Introduction

Now-a-days, single crystals are routinely grown by variety of techniques to satisfy the needs of science and modern technology. Organic materials have become a source of attraction to researchers because of their superior performance with respect to NLO properties such as large NLO coefficient and high optical damage threshold. The search for new and efficient NLO material has resulted in the development of the new class of materials called as organic mixed crystals. Non-linear optical materials (NLO) exhibiting second harmonic generation have been in great demand over the last few decades due to technological importance in the fields of optical communication, signal processing and instrumentation [1]. In recent years, the NLO properties of semi-organic complex products of thiourea have attracted great interest because these metal–organic complexes combine the high optical nonlinearity and chemical flexibility of organics with the physical ruggedness of inorganics. The thiourea molecule is an interesting inorganic matrix modifier due to its large dipole moment and its ability to form an extensive network of hydrogen bonds [2]. Thiourea compound crystals exhibit interesting optical, crystalline perfection, dielectric, mechanical and electronic properties reported by various authors are bis(thiourea) cadmium chloride, bis(thiourea) zinc chloride, bis(thiourea) cadmium acetate [3], bisthiourea zinc acetate [4], etc.

In the present investigation, a lot of studies have been carried out to explain the mechanism involved during the growth process. The growth mechanism incorporates the correlation of thermodynamics, kinetics and transportation factor to explain the behavior and morphology of the grown crystal in saturated solution. Nucleation process is the first and the most important phenomenon in liquid–solid transition. However, as per the authors knowledge, at present there is no literature available regarding the morphological and growth rate studies of thiourea mixed with cadmium iodide except the few reports like bis thiourea cadmium formate and bis thiourea cadmium chloride [5,6]. Thus, the aim of this paper is to describe the morphological and rate of growth of thiourea mixed with cadmium iodide crystal in two different ratios i.e. 2:1 and 1:1. During the formation of crystals, its live growth process and changing morphological features were recorded with the help of inverted microscope. The grown crystals were characterized by powder X-ray diffraction (PXRD), FT-Raman, UV–vis spectroscopy, field effect scanning electron microscopy (FESEM), TG/DTA and dielectric studies. Analyses of various results have been presented.

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## 2. Experimental details

### 2.1. Synthesis and crystal growth

Thiourea cadmium iodide (TCI) was synthesized by mixing aqueous solutions of thiourea and cadmium iodide in two different ratios (2:1) and (1:1). The synthesis of TCI was according to the following chemical reaction:

$$CdI_2 + 2[CS(NH_2)_2] = CdI_2(CH_4N_2S)_2 \text{ when TCI in } 2:1 \text{ ratio.} \quad (a)$$

$$CdI_2 + [CS(NH_2)_2] = CdI_2(CH_4N_2S) \text{ when TCI in } 1:1 \text{ ratio.} \quad (b)$$

Since thiourea has the coordination capacity to form different phases of metal–thiourea complexes, the mixtures of the reactants had to be stirred well to avoid the co-precipitation of multiple phases and also to get the homogeneous and transparent solutions [7]. TCI single crystals were grown by solution growth technique at ambient condition. The solution was made saturated by dissolving the synthesized TCI (2:1 and 1:1) in double distilled water in two separate good quality beakers. The temperature of the solution was raised up to 60 °C from room temperature by using 2MLH magnetic stirrer coupled with controlled heating to make the solution more saturated. At this temperature, the solution was continuously stirred for more than 12 h to get the homogenous and transparent mixture of supersaturated solutions. After preparing the solutions the temperature was slowly decreased to room temperature. About 40 ml filtered solution of each was taken in a Petri dish and focused to the camera attached with the inverted microscope. The remaining solutions were kept in constant temperature bath at room temperature to grow their single crystal and after one week the crystal were harvested from the mother solutions of size (7.3 mm × 3.0 mm × 1.5 mm) of TCI (2:1) and (6.0 mm × 2.0 mm × 1.0 mm) TCI (1:1) as shown in Fig. 1.

### 2.2. Characterization techniques

The morphology and intermediate growth stages of the grown crystal were observed with the help of inverted microscope (made by Motic) interfacing with the computer system. The pictures were captured with the help of a camera (Moticam 2300, 3.0 M pixel USB 2.0) attached to the microscope. We used objective lens of magnification PH 10×/0.25, ∞/1.1WD7.5 in our experiment. The PXRD of the grown single crystals was recorded by using PW1830 Philips analytical powder X-ray diffractometer with CuKα radiation (35 kV, 30 mA) and scanned with step size 0.02° for the angular range 5–50° of 2θ to know the crystal system and lattice parameters. Vibrational studies were carried out using FT-Raman spectrometer (Model Raman Station 400, Perkin Elmer) in the range of 3500–0 $cm^{-1}$ with 4 $cm^{-1}$ resolution. The optical transparency of the grown single crystal was checked by using Perkin Elmer lambda 35, UV–vis spectrophotometer in the range of 200–800 nm. The morphology and structure of the cleaved cross-section of both the single crystals was characterized with the help of a Scanning Electron Microscope made in JEOL Japan (Model-JSM-7600F). Thermal analysis was performed using the SII EXSTAR 6000 analyzer (Japan) from 40 °C to 600 °C in nitrogen atmosphere at 20 °C/min flow rate to identify the thermal stability, purity and crystalline nature of the grown crystals. The dielectric measurements were carried out using a precision LCR meter (Agilent 4284A) operating at oscillation amplitude of 1 V.

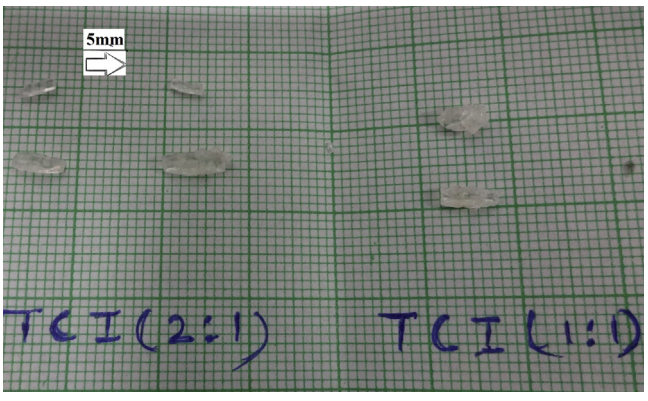


**Fig. 1.** Photograph of TCI (2:1) and TCI (1:1) as grown single crystals.

## 3. Results and discussion

### 3.1. Inverted microscope analysis

Fig. 2 shows the complete growth rate in sequence with the different morphologies of TCI in 2:1 and 1:1 ratio. The pictures placed in 1st row (No. 1) were just after the filtration of solution there is no crystal formation observed. Further, the pictures were captured at an interval of ~30 min by inverted microscope. This microscope is capable to capture the picture of micro size. For the first time well defined crystals are shown in 2nd row (No. 2) for both ratios 2:1 and 1:1.

Pictures represented in 3rd and 4th row (No. 3 and 4) of Fig. 2 show the continuous increment in the size of the crystal. From these pictures we can observe that the crystals of TCI grows in length wise as well as width wise also (i.e. two planer growth). We observe here the fast nucleation as well as the continues increment in crystal growth started from 0.1 μm to 2.0 μm along length and 0.01 μm to 1.0 μm along width in case TCI (2:1) ratio and in case of TCI (1:1) ratio along length wise the increment is 0.1 μm to 1.7 μm and along width wise 0.1 μm to 0.5 μm. It is clear that the growth rate in 2:1 is higher than 1:1 ratio. From Fig. 2 (No. 2 to 4) we observe increase in the size of the TCI crystals in both cases. In Fig. 2.4 the TCI crystals attains a good visible size of 2.0 μm × 1.0 μm in case of TCI (2:1) and 1.7 μm × 0.5 μm in case of TCI (1:1) crystals where both cases have similar crystalline morphology.

### 3.2. Powder X-ray diffraction analysis

PXRD patterns of TCI single crystals (a) 2:1 and (b) 1:1 are shown in Fig. 3. The pattern shown in Fig. 3(a) contains all the original peaks agreed well with the earlier reported bis thiourea cadmium iodide [7]. The revelation of well defined Bragg's peaks at specific 2θ as shown in the patterns proves the good crystallinity of the grown crystal. The Bragg's reflections were indexed for TCI (2:1) and TCI (1:1) single crystals and PXRD data was refined by 'CHEKCELL' software. The calculated and reported values of lattice parameters of TCI (Tables 1 and 2) are found to be very close to each other. Confirming the grown single crystals belongs to the monoclinic crystal system with space group of $P2_{1/c}$. The spectra shown in Fig. 3(b) of TCI (1:1) show no change in phase and also no additional peak was found in the PXRD patterns as compared to 2:1 ratio of TCI compounds. The obtained values of lattice parameters and PXRD data of TCI (2:1) and TCI (1:1) are found to be very similar to each other and with reported one. Since almost all the compounds can be grown by slow evaporation solution method, the compound can be synthesized by dissolving the salt in different stoichiometric ratios and by slowly evaporating the solution their crystal can be grown. This is a simple method of making the compound which leads to the expected new product, but sometimes the results are different like in case of Glycine Zinc chloride. Researchers have made this compound in three different