Asian Journal of Chemistry; Vol. 25, No. 2 (2013), 969-971

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.13274

Growth and Characterization of *Bis*(thiourea) Cadmium Acetate Single Crystal: An Efficient Semiorganic Non-linear Optical Single Crystal

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(*Received*: 14 December 2011; *Accepted*: 27 August 2012) AJC-12023

Bis(thiourea) cadmium acetate, a metal semiorganic non-linear optical crystal, was synthesized from thiourea and cadmium acetate using double distilled water. The synthesized salt was used to grow bulk size crystals. The XRD analysis confirmed that *bis*(thiourea)cadmium acetate has orthorhombic crystal structure. The UV transmission study indicates that there is a very low absorption in the visible light region. FTIR analysis suggests the presence of functional groups in the grown crystal. Thermal studies reveal that the grown crystal has considerable thermal stability and it can be exploited for industrial applications. The non-linear optical study confirms frequency doubling of the sample using Nd:YAG laser.

Key Words: *Bis*(thiourea) cadmium acetate, Single crystal, Growth, Non-linear optical crystal.

INTRODUCTION

In the last decade, organic nonlinear optical crystals with aromatic rings have attracted much attention because of their high nonlinearity, fast response and tailor made flexibility[1]. However, the shortcomings of aromatic crystals, such as poor physicochemical stability, low hardness and cleavage tendency hinder their device applications.

In order to keep the merits and overcome the shortcomings of organic materials, a class of non-linear optical crystals namely, organometallic or semiorganic crystals have been developed[2]. Ideally the large non-linearities of π-conjugated organics and the favourable crystal growth characteristics and mechanical properties of ionic salts can be combined into a single non-linear optical crystal[3]. Extended π-conjugated networks in organic systems with the largest nonlinearities invariably have significant absorption in the visible region of the spectrum[4]. Consequently, for SHG into the blue-near-UV regions, more transparent and less extensively delocalized organics must be considered (*e.g.*, urea) at the expense of decreasing the nonlinearity. 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. *Bis*(thiourea) cadmium acetate has been identified as an organometallic nonlinear optical crystal, which is a new semiorganic non-linear optical material synthesized by combining thiourea (which is typical polar molecule) with cadmium acetate[5].

EXPERIMENTAL

Synthesis and growth: *Bis*(thiourea) cadmium acetate (BTCA) salt was synthesized by dissolving thiourea and cadmium acetate taken in the molar ratio 2:1 in double distilled water. The reaction formula is:

$$Cd(CH_3COO)_2 + 2[CS(NH_2)_2] \longrightarrow Cd[CS(NH_2)_2]_2{\cdot}(CH_3COO)_2$$

Solubility of *bis*(thiourea) cadmium acetate in double distilled water was determined at different temperatures (30, 35, 40, 45 and 50 ºC) with continuous stirring. After attaining the saturation, the equilibrium concentration of the solute was estimated gravimetrically. The solubility curve of *bis*(thiourea)-cadmium acetate is shown in Fig. 1.

The saturated solution of *bis*(thiourea) cadmium acetate was carefully prepared using double distilled water based on the solubility data. The solution was continuously stirred for 2 to 3 days in order to maintain uniform concentration gradient in the crystallizer. After stirring the solution, it was filtered and transferred to a 250 mL beaker covered with perforated plastic thin sheet. The solution was allowed to evaporate at 305 K.

Due to spontaneous nucleation seed crystals were seen within the period of 7 to 10 days. Transparent good quality seed crystals with perfect shape and free from macro defects were taken and immersed in the mother solution using nylon

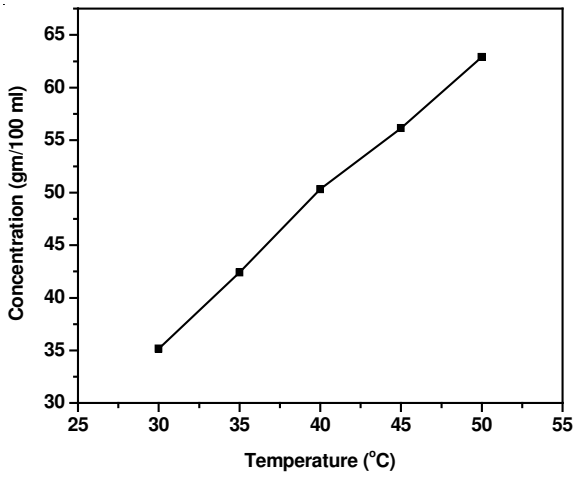

Fig. 1. Solubility curve for *bis*(thiourea) cadmium acetate

thread. Single crystal of size upto 19 mm × 8 mm × 7 mm was harvested in a period of 25 to 30 days and Fig. 2 shows the photograph of the as grown crystal of *bis*(thiourea) cadmium acetate. The crystal is highly transparent and free from visible inclusions.

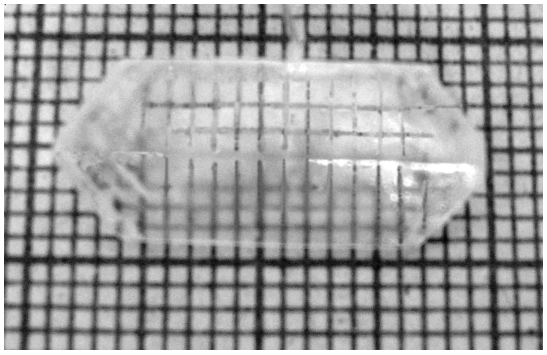

Fig. 2. Photograph of *bis*(thiourea) cadmium acetate single crystal

Single crystal X-ray diffraction analysis: *Bis*(thiourea) cadmium acetate crystal structure was studied using single crystal X-ray diffraction analysis. The *bis*(thiourea) cadmium acetate crystal falls under orthorhombic crystal structure and values of the cell parameters are presented in Table-1. The observed data agrees well with the earlier work[5].

TABLE-1
CRYSTAL DATA OF *BIS*(THIOUREA) CADMIUM ACETATE SINGLE CRYSTAL

Crystal formula	$Cd[CS(NH_2)_2]_2{\cdot}(CH_3COO)_2$
Crystal system	Orthorhombic
a (Å)	7.5854 (3)
b (Å)	11.8195 (4)
c (Å)	15.5043 (3)
V $(Å)^3$	1390.05 (4)
$\alpha = \beta = \gamma$	90°

RESULTS AND DISCUSSION

The FTIR spectral analysis of *bis*(thiourea) cadmium acetate reveals the effect of coordination on vibrational bands of the ligand in the metal complex. Fig. 3 shows the 4000-400 cm^{-1} region in the FT-IR spectrum of *bis*(thiourea) cadmium acetate. In the high wavenumber region 300-3400 cm^{-1}, there are several peaks due to N-H stretching. A comparison of *bis*(thiourea) cadmium acetate wavenumbers with thiourea is presented in Table-2. The peaks at 1495 and 1110 cm^{-1} are due to CN asymmetric and symmetric stretching vibration, respectively. The peak at 1412 cm^{-1} is attributed CS asymmetric stretching vibration. The CS symmetric stretching vibration is observed at 725 cm^{-1}. The other modes of vibrations of *bis*(thiourea) cadmium acetate are assigned and presented in the same table. It is evident from the spectrum of *bis*(thiourea) cadmium acetate, that the CN stretching vibrations of thiourea are shifted to higher frequencies whereas, the CS stretching vibrations of thiourea are shifted to lower frequencies. Hence, thiourea has coordinated to the cadmium through sulphur in *bis*(thiourea) cadmium acetate.

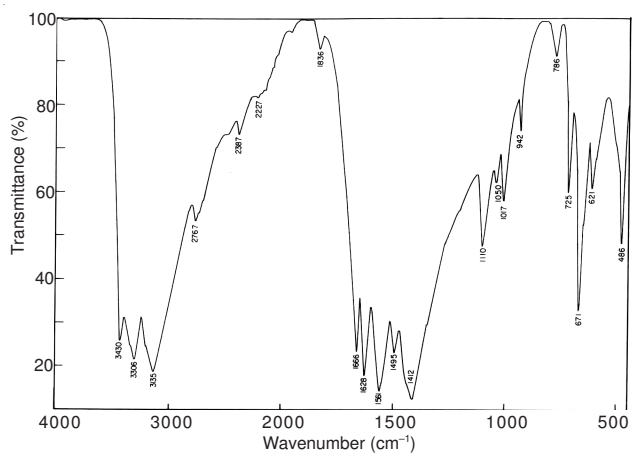

Fig. 3. FTIR spectrum of *bis*(thiourea) cadmium acetate

TABLE-2
WAVENUMBER ASSIGNMENT OF *BIS*(THIOUREA) CADMIUM ACETATE (BTCA) WITH THIOUREA

Wavenumber (cm^{-1})		Assignment
Thiourea	BTCA	
3380, 3279, 3090	3430, 3306, 3135	N-H Stretching vibrations
1627	1666	NH_2 Asymmetric stretching
1472	1495	CN- Asymmetric stretching
1417	1495	CS- Asymmetric stretching
1089	1110	CN-Symmetric stretching
740	725	CS- Symmetric stretching
640	621	NCS- Asymmetric bending
494	486	NCS- symmetric bending

Optical transmission studies: The optical transmission range and the transparency cut-off are important for NLO materials. The optical transmission spectrum of *bis*(thiourea) cadmium acetate was recorded using a HITACHI U-2010 spectrophotometer in the range 200-1100 nm and is shown in Fig. 4. It is evident from the spectrum that *bis*(thiourea) cadmium acetate has high percentage of transmission in the entire visible region. The UV transparency cut-off wavelength of grown crystals occurs below 290 nm, which is expected to provide a better range of applications.

NLO test: For the SHG efficiency measurements, microcrystalline material of KDP was used for comparison Kurtz *et al.*[6]. When a laser input of 6.2 mJ was passed through *bis*(thiourea) cadmium acetate, second harmonic signal of 532 nm

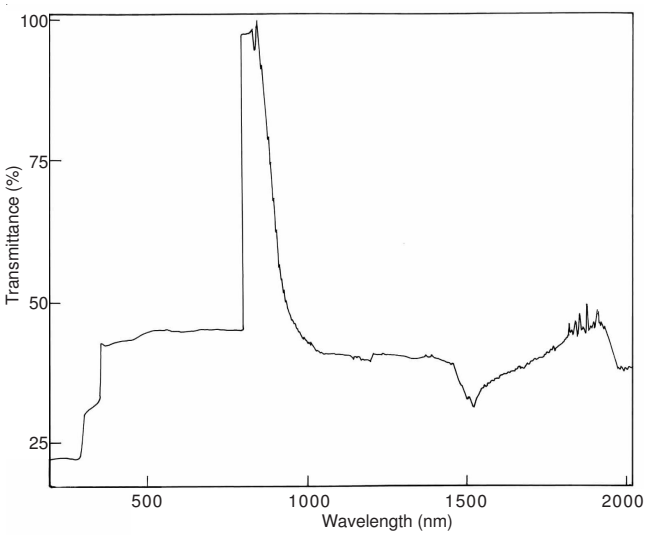

Fig. 4. Optical transmission spectrum of *bis*(thiourea) cadmium acetate

is produced. The second harmonic signal of 192 mV was obtained for *bis*(thiourea) cadmium acetate with reference to KDP (275 mV). Thus the SHG efficiency of *bis*(thiourea) cadmium acetate crystal is nearly 0.7 times than KDP.

Thermal studies: The TG-DTG traces of *bis*(thiourea) cadmium acetate were recorded between 20 to 1000 ºC at a heating rate of 20 K/min. using SDT Q600 thermal analyzer. The experiment was performed in nitrogen atmosphere. The resulting thermograms are shown in Fig. 5, which suggest

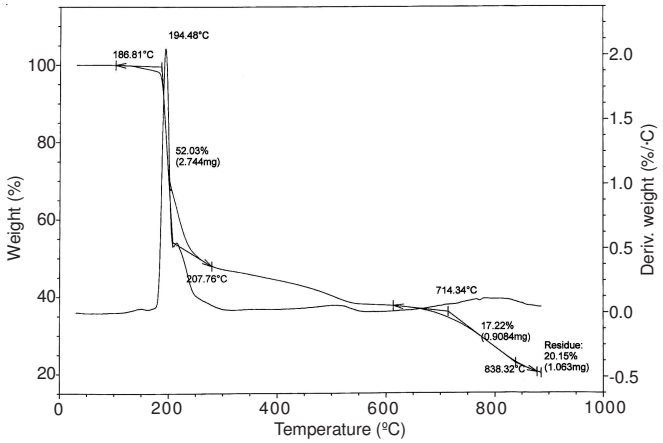

Fig. 5. TG-DTG traces of *bis*(thiourea) cadmium acetate single crystal

nearly 2 stages of decomposition. The maximum decomposition temperature occurs at 194.48 ºC, which may be due to the removal of hydrogen from the thiourea molecules. During the first and second stages of decomposition, the weight losses are found to be 52.03 and 17.22 %, respectively. The final residue is found to be 20.15 % at 886 ºC. Hence, the grown crystal is thermally stable up to 194.48 ºC.

Conclusion

Single crystals of *bis*(thiourea) cadmium acetate were grown from aqueous solution at room temperature. Solubility of *bis*(thiourea) cadmium acetate was investigated for double distilled water. Bulk crystals were grown by slow evaporation method. Crystal of size 19 mm × 8 mm × 7 mm is grown with reasonable growth rate. The structure of *bis*(thiourea) cadmium acetate was confirmed by single crystal XRD. FTIR studies ascertain the coordination of sulphur with metals. The transmission spectrum of this crystal shows a high transmission in the visible region. Second harmonic generation of *bis*(thiourea) cadmium acetate was confirmed by Kurtz powder technique. Thermal studies reveal that the grown crystal undergoes two stages of decomposition.

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