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Synthesis, Growth, Structural, Spectroscopic, Thermal and Optical Properties of Semiorganic Material-Tristhiourea Cadmium Sulphate (TTCS)

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ABSTRACT

Single crystal of tristhiourea cadmium sulphate (TTCS) was grown by slow cooling technique. Grown crystals have been characterized using single crystal XRD, Fourier Transform Infrared (FTIR) and Raman spectroscopy, TGA/DTA, UV-vis-NIR and etching studies. Optically transparent and defect free single crystals of size up to 13×08×07 mm^3 were harvested in a period of 25 days. Presence of different functional groups in the TTCS crystal was discussed through FTIR and Raman spectra. Transmittance of the crystal revealed that the crystal suitable candidates for optoelectronic applications. The thermal character of TTCS was analyzed by TGA/DTA.

Keywords: Thiourea, Characterization, X-ray diffraction, Growth from solutions, Nonlinear optical material

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INTRODUCTION

Nonlinear optical (NLO) materials find wide applications in the field of telecommunications, optical information, frequency conversion and laser technology. Science and technology are in need of more and more new materials, especially in electronics, computers and information technology. Several properties like optical, nonlinear optical, dielectric, magnetic, laser action, super conducting, photoluminescence, photo conduction, photo refraction etc. have much significance in these technologies. Semi organic crystals have the advantages of both organic and inorganic properties. They possess large optical non-linearity, high resistance, good optical properties and mechanical strength when compared to inorganic and organic crystals. The metal organic complexes are in great attention in nonlinear optical field [1-4]. Among the semi organic nonlinear optical materials, metal complexes of thiourea which have low UV cut off wavelengths, applicable for high power frequency conversion have received much attention. Thiourea is an interesting organic compound due to its ability to form extensive hydrogen networks with metals [5-7]. The centrosymmetric thiourea molecule, when combine with inorganic metal compound gives metal organic complexes, which has the nonlinear optical properties. Bis thiourea cadmium chloride, Copper thiourea chloride, Zinc (tris) thiourea sulphate, Bis thiourea zinc chloride, Bis thiourea cobalt chloride, Tetra thiourea copper chloride, Tris (thiourea) cadmium sulphate are some of metal organic coordination of thiourea compounds. A new type of thiourea metal complex, tristhiourea cadmium sulphate (TTCS) was synthesized by S.Dhanuskodi et al [8] using chemical reaction method. In this paper, some more characterization of the TTCS crystals are reported along with the earlier studies.

MATERIALS AND METHODS

2. Experiment

2.1 Synthesis and crystal growth:

Tris thiourea cadmium sulphate (TTCS) can be synthesized based on following stoichiometric equation using Merck grade cadmium sulphate and thiourea.

$$CdSO_4 + 3[CS(NH_2)_2] \rightarrow [Cd(CS(NH_2)_2)_3]\ SO_4$$

The synthesized salt was subjected to recrystallization. Using the purified salt a saturated solution was prepared. From this a good morphological seed crystals were collected by spontaneous nucleation process. The seed crystal was hanged in a saturated solution prepared at 40^{o}C and placed in a constant temperature bath (CTB) with an accuracy of ± 0.01 ^{o}C. Bulk crystal was grown by slow cooling technique (0.1^{o}C per day). The well transparent crystal was harvested after 25 days from the solution. Single crystals of TTCS is shown in the Fig. 1.

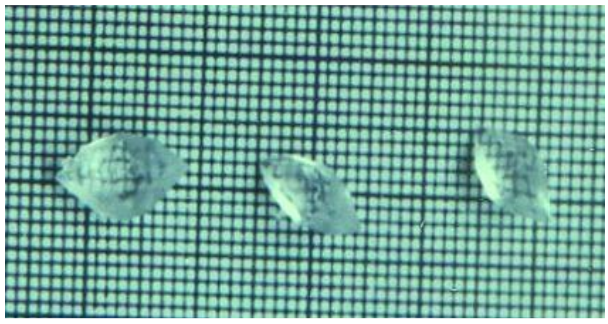

Fig. 1 Photograph of TTCS crystal

2.2 Characterization

The structure of the grown crystals was examined by single crystal XRD using Enraf Nonius CAD-4 diffractometer with MoKα (λ= 0.1770 Å) radiation and also estimated the lattice parameters values. Nucleation mode and surface orientation was observed through etching studies. The presence of functional groups and the coordination of metal-thiourea ligand are confirmed by FT-IR spectroscopy using Perkin Elmer spectrometer. FT-Raman spectrum has been recorded using Thermo electron corporation Nexus 670 spectrometer in the range 3701–100 cm^{-1}. TGA/DTA were carried out using the instrument NETSZCH SDT Q600 V8.3 Build 101 at a heating rate of 20^{0}C/min in nitrogen atmosphere in temperature range 0^{o}C –1200^{o}C.

RESULTS AND DISCUSSION

Table 1. Unit cell parameters of TTCS.

Parameters	Thiourea [10]	TTCS [9]	TTCS [present work]
Empirical formula	$CS(NH_2)_2$	$[Cd(CS(NH_2)_2)_3]\ SO_4$	$[Cd(CS(NH_2)_2)_3]\ SO_4$
Crystal system	Monoclinic	Triclinic	Triclinic
α	90.0	91.3	91.58
β	90.66	111.9	110.51
γ	90.0	95.5	95.77
a (Å)	9.701	9.05	9.069
b (Å)	5.261	8.77	8.766
c (Å)	11.953	9.83	9.682
cell volume (Å^3)	610.044	718.9	769.70

3.1 Structural studies

Single crystal X-ray diffraction analysis was carried out using an Enraf CAD-4 diffractometer with MoKα (λ= 0.7170 Å) radiation to indentify the structure and to estimate the lattice parameter values. From the analysis the structure of the grown crystal was confirmed to be a triclinic with cell parameters a=9.069 Å, b=9.682 Å, c=8.766 Å

and α=110.51°, β=95.77° γ =91.58°. The lattice parameters evaluated from the single crystal X-ray diffraction are in good agreement with that of earlier report [9]. The comparison of unit cell parameters of TTCS crystal with thiourea is shown in Table 1.

3.2. Fourier Transform Infrared (FTIR) and Raman studies

FTIR and Raman spectra of TTCS are shown in Fig. 2&3. In TTCS complex, there are two possiblilities by which the coordination of cadmium with thiourea may occur either through nitrogen or sulfur of thiourea. The broad envelop in between 3000 to 3500 cm^{-1} corresponds to the symmetric and asymmetric stretching modes of NH_2 group. The strong band observed at 1621 cm^{-1} is assigned to NH_2 assymmetric bending. The band at 1408 cm^{-1} corresponds to the C-S asymmetric stretching. Strong peak at 483 cm^{-1} shows clearly that N-C-N bending vibration. The appearance of bands at 618 and 967 cm^{-1} show asymmetric bending and symmetric stretching for SO_4^{2-} ion. Very intense peak at 706 shows the C-N asymmetric stretching. From the comparison of thiourea, the peak shift from 1477 to 1500 cm^{-1} confirms metal sulphur coordination because the appearance of double bond character for the C-N bond. The appearance of peaks 3233 to 3052 cm^{-1} and the band at 1649 in Raman spectrum further confirm the presence of functional group NH_2 stretching and asymmetric bending vibration. The peaks at 483, 610, 720, and 1481 cm^{-1} corresponds to the C-N vibrational frequencies. They are appeared as in FTIR spectrum with slight variations. 632 and 974 cm^{-1} is assigned to SO_4^{2-} symmetric stretching. The band appears at 212 cm^{-1} confirms the Cd-S stretching coordination bond. The appearance this peak confirms the metal-sulphur coordination in the TTCS complex crystal. The above assignments are based on the work of Refs [10-12]. The assigned peaks are shown in the table 2.

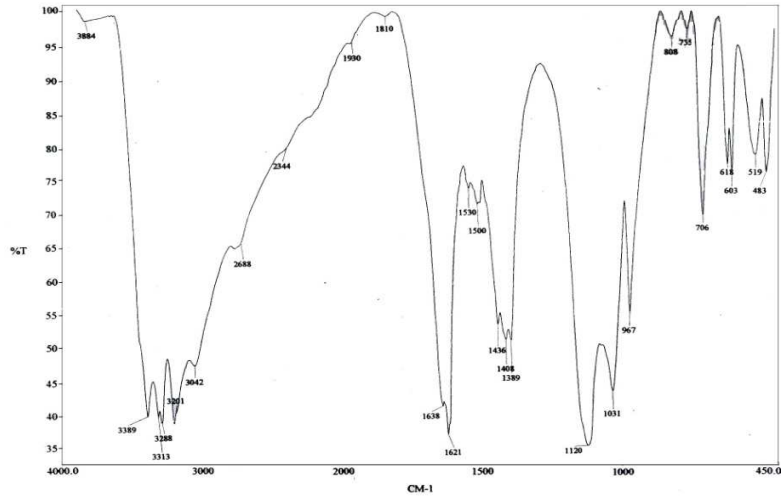

Fig. 2 FTIR spectrum of TTCS crystal

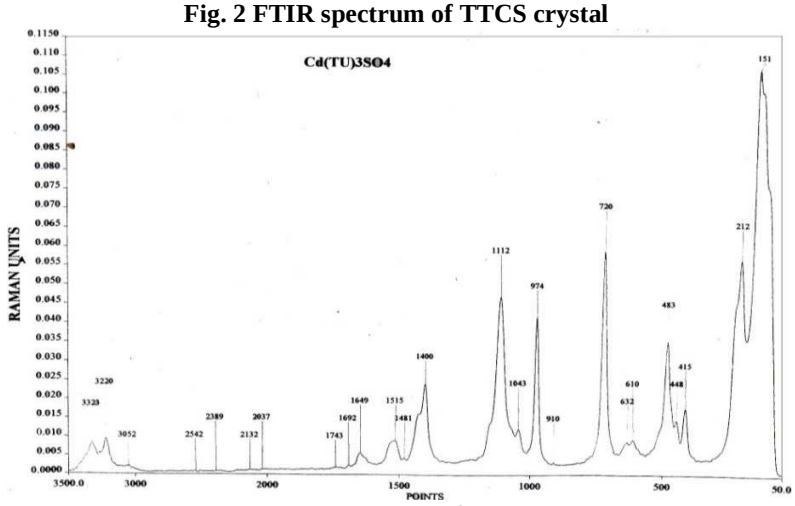

Fig. 3 Raman spectrum of TTCS crystal

Table 2. Functional group assignments of TTCS.

FTIR	RAMAN	Assignments
	212	Stretching of Cd–S
483	483	N-C-N bending vibration
519		Bending of C-N
603	610	Bending of C-N
618	632	asymmetric bending of SO_4^{2-}
706	720	C=S stretching, C-N symmetric stretching
967	974	symmetric stretching of SO_4^{2-}
1031	1043	COH Stretching
1120	1112	Torque of (NH_2)
1408	1400	C-S asymmetric stretching
1500	1481	C-N assymetric Stretching
1621		NH_2 bending
1638	1649	NH_2 bending
3042	3052	Symmetric and asymmetric Stretching of NH_2
3201	3220	Symmetric and asymmetric Stretching of NH_2
3288		Symmetric and asymmetric Stretching of NH_2
3313	3323	Symmetric and asymmetric Stretching of NH_2
3389		Symmetric and asymmetric Stretching of NH_2

3.3 Optical transmission studies

Optical transmittance spectrum of the grown crystals is shown in Fig. 4. From the spectrum, it is evident that TTCS crystal has UV cut off around 300 nm and there is no major absorption in the visible and near IR region. The increased transparency in the visible region enables the achievement in use of optoelectronic devices.

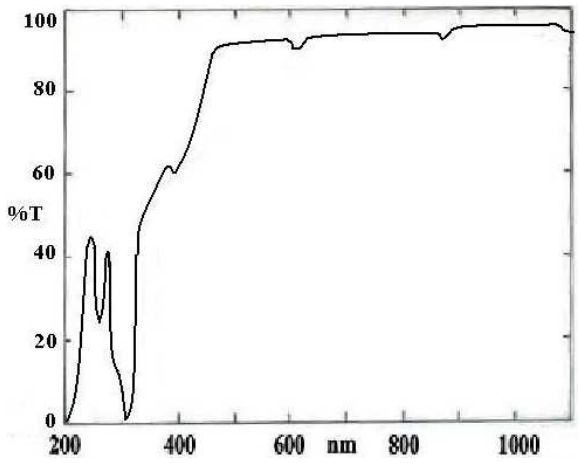

Fig. 4 Optical transmittance of TTCS crystal

3.5 Thermal studies

The thermal stability of the grown crystals was analyzed by thermo gravimetric (TGA) and differential thermo gravimetric (DTA) analysis with the heating rate of 2.5°C/min under the nitrogen atmosphere. TGA and DTA spectra of the grown crystal are shown in the figure 5. The first weight loss occurs at 221°C due to the removal of the hydrogen atom. The remaining stages of the weight loss are due to the decomposition of thiourea into nitrogen, sulphur and carbon. After all the decomposition the residual material was found to be cadmium. Thus TTCS is thermodynamically stable upto 221°C. A sharp endothermic peak at 276°C in DTA is melting point of the compound TTCS. The material which undergoes decomposition before its melting point thus growth in aqueous solution is only favorable.

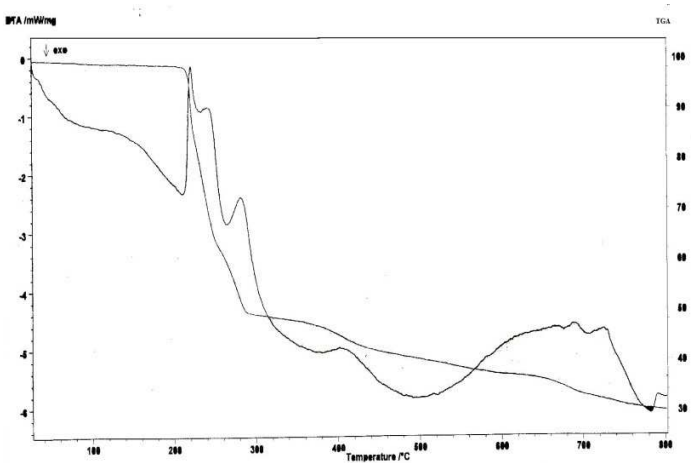

Fig. 5 TGA/DTA traces of TTCS crystal

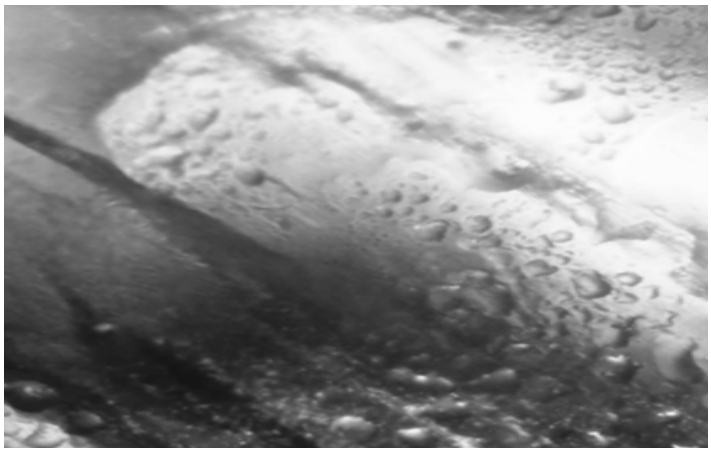

Fig. 6 Etch pattern of TTCS crystal

3.6 Etching Studies

The etching studies expose the structural perfection and lattice defects of grown crystals. The surfaces of samples were polished and then etched in the etching solution at room temperature for 10s. An optical microscope in reflection mode examined the crystal. Fig. 6 illustrates the etch pattern observed on the (001) plane.

CONCLUSION

The lattice parameters evaluated from the single crystal X-ray diffraction are confirm that the grown crystal is tristhiourea cadmium sulphate and the crystal is belongs to triclinic system. FTIR and Raman studies reveal that various functional groups of the crystal and their vibrational interactions. The UV-Vis-NIR spectral study highlights the excellent transparency of the crystal in the visible and near infrared region. TGA and DTA analyses reveal the different stages of decomposition and stability of the crystal.

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