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STRUCTURAL AND MECHANICAL PROPERTIES OF TRIS (THIOUREA) CADMIUM SULPHATE

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ABSTRACT: **Semi-organic nonlinear optical Tris(thiourea) cadmium sulphate (TTCS) single crystals were grown by slow evaporation method. The crystal system and cell parameter of the grown crystal were identified by powder X-ray diffraction study. By this study the dislocation density and strain values of the lattice were estimated. The mechanical property of the grown crystal was examined by using Vickers micro hardness test. The functional groups present in the grown crystals were ascertained using FTIR and FT-RAMAN spectroscopic analysis. Chemical etching studies were made on the TTCS crystal using water as an etchant. The dark and photocurrent property of the crystal was estimated by using photoconductivity study.**

KEYWORDS: **Structural properties; Optical properties; Microstructures; Mechanical properties;**

1. INTRODUCTION

Semi-organic nonlinear optical (NLO) materials have a significant impact on laser technology, optical communication and is applied in optical storage technologies in recent years [1-2]. The organic materials have large NLO co-efficient when compared to inorganic materials, but their usage is impeded due to their poor mechanical strength, low thermal stability and low laser damage threshold [3]. This organic molecular salt exhibits interesting NLO properties because of its strong Coulomb interactions in charged molecules [4].The inorganic materialshave excellent mechanical and thermal properties, but possess relatively modest optical nonlinearities, due to lack of extended π-electron delocalization [5]. Materials which have both the high nonlinear optical efficiency and stability reveals the interest for future technological advancements. These semi-organic materials are great materials for second and third-order nonlinear optical applications. The solution growth technique is an efficient way to produce good quality semi organic NLO crystals [6]. One such semi-organic material is the metal complex of thiourea. The thiourea molecule is an interesting inorganic matrix modifier since it has a large dipole moment. It has the good ability to form an extensive network of hydrogen bond and has the co-ordination capacity to form different phases of metal–thiourea complexes [7-8]. In our study, thiourea a typical polar molecule is selected to combine with cadmium sulphate and its results are summarized.

2. EXPERIMENTALWORK

The semi-organic nonlinear optical compound Tris(thiourea) cadmium sulphate (TTCS) was synthesized by direct chemical reaction. A calculated amount of AR grade thiourea (3mol%), and cadmium sulphate (1mol%) wasdissolved in deionized water. These mixtures of reactants were stirred well for about 6 h to avoid co-precipitation of multiple phases. The synthesized solution produced TTCS salt and its purity was improved by repeatedrecrystallization processes in aqueous solution. This purified salt was then used to prepare saturated TTCS solution that was further stirred well, and filtered with high quality filter paper to avoid any impurity. The saturated growth solution was poured into a container and isolated by inciting

slow evaporation of the solvent. After 3 weeks, the supersaturated mother solution yielded the spontaneous nucleated TTCS crystals . The well-grown TTCS crystals were harvested in a period of 4-5 weeks. The optically transparent TTCS crystals, whose dimensions upto 10 x 5 x 4 mm3 were obtained as shown in Fig.1. The good quality crystals were used for further characterizations.

Fig.1 Grown TTCS crystal by slow evaporation method

3. CHARACTERIZATION

$CdSO4 + 3[CS(NH2)2] \rightarrow [Cd(CS(NH2)2)3]\ SO4$

X-ray powder pattern of the crystal was recorded on a SIEFERT X-ray Diffractometer using Cukα(Kα = 1.540598) radiation.The grown single crystals of TTCS was confirmed by single crystal X-ray diffraction analysis . Microhardness measurements were measured using a Leitz Matallux II microscope with a calibrated ocular at X500 magnification based on Vickers's micro hardness method . The FTIR and FT-RAMAN spectrum of TTCS crystal were recorded in the region 400-4000 cm-1 Microstructure analysis was carried out on the crystal by using an optical microscope in the reflective mode .The photoconductivity was measured using a Keighley Pico ammeter between 0 to 2800 volt/cm.

4. RESULTS AND DISCUSSION

4.1 X-RAY DIFFRACTION STUDY

The powder X-ray diffraction pattern of TTCS crystal isrecorded by SIEFERT X-ray diffractometer using Cukα (Kα=1.54) radiation. The recorded pattern of TTCS crystal is shown in Fig.2. The disclosure of well-defined Bragg's peaks at specific 2θ angle shows the high crystallinity of TTCS crystals. The value of 'd' spacing is calculated using Bragg's equation. The dislocation density (δ) and strain values (ε) were estimated using the Scherrer equation [9],

$$\tau = \frac{K\lambda}{\beta \cos\theta} (1)$$

where K is the shape factor of a value of 0.94, λ is the wavelength of the incident X-ray beam, β is FWHM in radians and 'θ' is the Bragg's angle. The strain, dislocation density (ε) was calculated using the following relations [10-12],

$$\text{Strain } (\varepsilon) = \frac{\beta \cos\theta}{4} (2)$$

$$\text{Dislocation density } (\delta) = \frac{1}{\tau^2} (3)$$

The FWHM was shown to increase with increase in dislocation density (δ), and increase in strain value (ε). Its estimated values were presented in Table 1. The cell parameters of the as-grown TTCS single crystals were evaluated and the values belonged to triclinic system of centrosymmetric $\overline{\mathbf{P_1}}$ space group, with cell dimensions of, a = 8.71 Å, b = 9.04 Å, c = 9.73 Å, α = 91.76o, β = 110.58o, γ = 95.55o, and volume (V) = 713 Å3. The observedcell values agreed with reported values [13-14].

Table1.

S.No	FWHM	Dislocation ensity(δ) $(L / l^3)\ m^{-2}$	Strain values (ε)
1	0.0800	3.305771×10^{-19}	0.019904
2	0.1200	6.651344×10^{-19}	0.029515
3	0.1600	10.924319×10^{-19}	0.037825

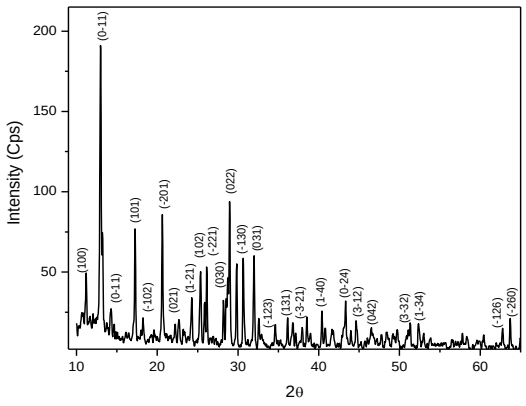

Fig.2 Powder X-ray diffraction pattern of TTCS crystal

4.2 VICKER'S MICROHARDNESS TEST

The hardness property of the crystals play a key role in device fabrication.The transparent crystals, free from cracks were selected for microhardness measurement. Microhardness test for the grown crystals were carried out using a Leitz Matallux-II microscope with a calibrated ocular at the magnification of 'X500'. Vicker's microhardness study had been used to analyze the hardness property of the grown TTCS crystals using a LEITZ microhardness tester fitted with a diamond pyramidal indenter. A well-polished TTCS crystal was used for the study and it was placed on the platform of Vickers microhardness .The loads (P) at different magnitudes were applied over a fixed interval of time with an indentation time of 8 s for all the loads. The hardness number was calculated using the relation,

$$H_V = 1.8544 \frac{P}{d^2} Kg/mm^2 \qquad (4)$$

where 'Hv' is the Vicker's microhardness number, 'P' is the applied load in 'Kg' and'd' is the diagonal length of the indentation impression. The plot between hardness number (Hv) and applied load (P) is shown in Fig.3(a) and it shows that hardness number decreases with increase in applied load. The Meyer's index (n) is used to determine if the material belonged to soft category or hard. According to Onitsch [15], the value (n) ranges between 1-1.6 for hard materials is greater than 1.6 for soft materials. TheMeyer's index number is calculated using Meyer's law,

$$P = Kd^n \quad (5)$$

$$\text{Log } P = \text{Log } k + n \text{ Log } d \quad (6)$$

Where 'k' is the constant for a material and 'n' is the Meyer's index. In order to find the value of 'n', a graph was plotted between applied loads 'log P' and 'log d', which resulted in the formation of a straight line. The slope value of the plot in Fig 3b was identified as n=1.753, thus confirming that the TTCS crystal belonged to soft category.

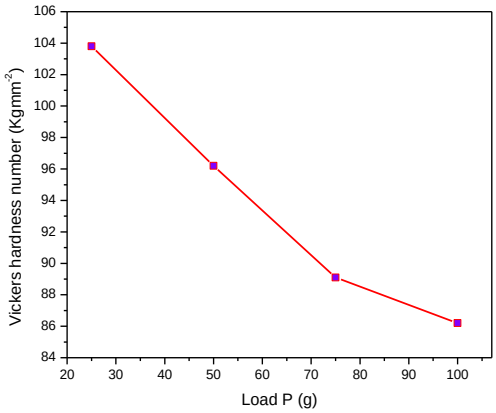

Fig.3 (a) Variation of Vicker's microhardness number (HV) with applied load (P) for TTCS Crystal.

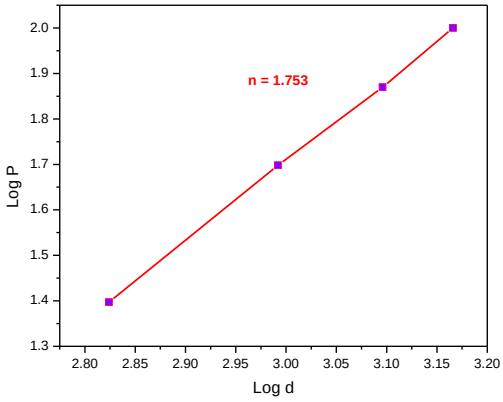

Fig.3(b) Variation between log P vs log d of TTCS crystal

4.2.1 FRACTURE TOUGHNESS, BRITTLE INDEX AND YIELD STRENGTH

The fracture toughness (Kc) describes the ability of a material containing a crack to resist fracture. The Kc determines how much fracture stress is applied under uniform loading. It is an important parameter for the

selection of materials for application where the load exceeds the limit or yield point [16] The expression for crack propagation under loading condition is determined by the analysis of the deformation fracture mechanics of the indentation process and it can be represented under equilibrium conditions [17] as

$$K_c = P / l^{3/2} \beta_0 \quad (7)$$

Where Kc is in (g/μm3/2), C in microns and β0 is the indenter constant, taken as 7 for Vickers diamond indenter. The elastic stiffness constant (C11) has been calculated using Wooster's empirical relation [18].

$$C_{11} = H_v^{7/4} \quad (8)$$

Brittleness is another important property of a crystal which determines its fracture without any appreciable deformation. The brittle nature of a crystal helps in understanding its laser damage tolerance. It is expressed in terms of brittleness index Bi (μm)-1/2 [19] and it is computed using the relation:

$$B_i = H_v / K_c \quad (9)$$

From the hardness value, the yield strength (σ_y) has been calculated using the relation [20]

$$\sigma_y = \frac{H_v}{3} (0.1)^{n'-2} \quad (10)$$

The calculated values are shown in table.2.

Table2.Mechanical parameter of TTCS crystal

LOAD g	HV	KC g/mm$^{3/2}$	Bi mm$^{-1/2}$	Yield kg mm^{-2}	C11
25	103.8	2.380952381	43.596	6.152846759	3375.556
50	96.2	4.761904762	20.202	5.702349308	2954.992
75	89.1	7.142857143	12.474	5.281489848	2583.961
100	86.2	9.523809524	9.051	5.109589505	2438.584

4.3. FT-IR STUDIES

The FTIR and FT-RAMAN spectra of TTCS areshown in the Fig 4.In TTCS, there are two possibilities by which the co-ordination of cadmium with thiorea can occur. The co-ordination with the cadmium may occur either through nitrogen or through sulphur of thiourea[21]. The study of the spectra of thiourea and its metal complex shows a shift in the frequency band in the low-frequency region. The characteristic vibrational frequencies of the functional groups of TTCS is compared with pure thiourea[22]. The band at lower frequency 504 cm-1 in FTIR and 478 cm-1 in FT-RAMAN corresponds to 494 cm-1 in pure thiourea is attributed to N-C-N bending vibration. The sharp and intense absorption of TTCS at 713 cm-1 in FTIR and 708 cm-1 in FT-RAMAN corresponds to the 713cm-1 absorption in thiourea. The lowering of frequency can be attributed to the reduced double bond character of the C=S bond on the co-ordination .The absorbtion band at 1408 cm-1 in FTIR and 1433 cm-1 in FT-RAMAN for TTCS corresponds to 1417 cm-1 of thiourea can be assigned to C=S stretching . The absorption bands observed at 1622 cm-1 in FTIR and 1543 cm-1 in FT-RAMAN of TTCS corresponds to 1622cm-1 of thiourea [23] and can be assigned to the NH2 bending vibration. The high frequency absorbtion bands 3288 cm-1 in FTIR and 3227 cm-1 in FT-RAMAN of TTCS corresponds to 3280 cm-1 in pure thiourea [24] is attributed to NH2 bending vibration. The broad envelope positioned in between 2750 cm-1 and 3500 cm- 1 corresponds to the symmetric and asymmetric stretching modes of NH2 grouping of cadmium-coordinated thiourea. The bonds of thiourea are not shifted to lower frequencies on the formation of the cadmium-thiourea complex. The increase in the frequency can be attributed to the greater double bond character of the carbon to the nitrogen bond on complex formation. The absorbtion bands of FTIR and FT-RAMAN spectra of TTCS crystal is tabulated in table3.

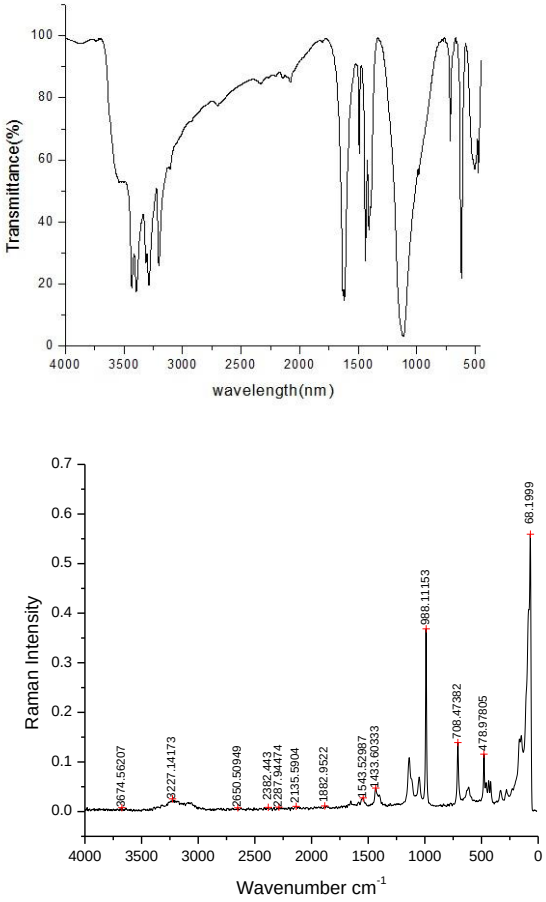

Fig.4 The FTIR and FT-RAMAN spectra of TTCS crystals

TABLE . 3 Comparison of FTIR AND FT-RAMAN bands of TTCS with thiourea

Thiourea	FTIR	FT-RAMAN	Assignments
494	504	478	N-C-N stretching
730	713	708	C =S stretching
1116	1116	-	N-C-N stretching
1417	1408	1433	C =S stretching
1625	1622	1543	NH2stretching
3167	3202	-	NH2 stretching
3280	3288	3227	NH2stretching

4.4 CHEMICAL ETCHING

The NLO property of the crystal purely depends on the perfection of the grown crystal. Microstructure analysis was carried out on the grown crystal by using optical microscope in the reflective mode. The well-polished crystal was used for surface treatment using water an etchant for 10 seconds. The atoms at the grain boundaries are chemically more active; consequently dissolve more readily, than those within the grain forming small grooves. The grooves become discernible when viewed under microscope because of reflected light with different angle. The recorded etch pit pattern of TTCS crystal is shown in Fig.5 in the scale of 100 μm.From the etch pit image, it is revealed that etch pit pattern in TTCS crystal growth is rod shaped.

Fig.5 Etchpit pattern of TTCS crystal with water in 10 s

4.5 PHOTOCONDUCTIVITY STUDIES

Photoconductivity is the incremental change in the electrical conductivity of a substance upon illumination which is generated by the absorption of photons [25]. The relevant photo excitation of free carriers and photoconductivity is expected when the crystal is illuminated with visible or near-infrared wavelengths. The polished, defect-free TTCS crystal sample which was rectangular in size was used for the study. Photoconductivity property of the grown TTCS crystal was measured in the range of 0-2800 V/cm

using a KEITHLEY picoammeter. The electrical contacts were made with the sample by silver paint and it was connected by copper wire which was used as an electrode. The light from halogen lamp of 100 W was focused on the sample using convex lens. In addition, the applied voltage was increased from 0-2800 V and the corresponding photocurrent was measured with respect to the applied voltage. The variations of photocurrent (IP) and dark current (Id) with applied field was shown in Fig.6. It was observed that both dark and photocurrents of the crystals increases linearly with the applied electric field but if the dark current is less than the photocurrent, photoconductivity of the TTCS crystal is positive.

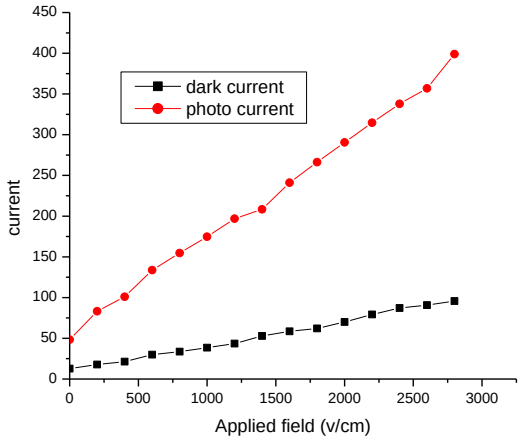

Fig.6 Photoconductivity measurement of TTCS crystal

5. CONCLUSION

Semi-organic thiourea metal complex Tris(thiourea) cadmium sulphate single crystals dimension upto 10 x 5 x 4 mm3 were grown by slow evaporation technique.The powder X-ray diffraction study confirmed the cell dimension, the dislocation density and strain values of thelattice.The hardness property of the crystal was studied and its Meyer's index value n= 1.753 suggested that TTCS is a soft material. The functional group was confirmed by FT IR and FT-RAMAN spectrum.The microstructure of the growth pattern was analyzed using etchpit study. The higher photocurrent was observed than the dark current value for different applied fields.

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