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Synthesis, Growth and Characterisation of New Tris Thiourea Cadmium Sulphate (TTCS) Crystal

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Abstract

TTCS single crystals have been grown successfully by slow evaporation technique from aqueous solution at room temperature. The functional groups present in the grown material have been confirmed by FTIR analysis. In order to find the lattice parameters the single crystal x-ray diffraction analysis has been taken. The crystalline nature of the material is determined with the help of powder x-ray diffraction patterns, whereas, the lattice parameters are found out by single x-ray diffraction analysis. The Second Harmonic Generation (SHG) test has been done to reveal the NLO property of the grown crystals. The mechanical properties of the grown TTCS crystal were studied by Vicker Hardness test. TGA/DTA curves establish the thermal properties of the grown crystal. UV-visible spectrum confirms that the crystal has lower cut-off in the uv region and higher cut-off frequency in the mid-IR region. TTCS is another new potential semi organic nonlinear optical material having better nonlinearity and a low UV cut-off.

Keywords: Dielectric Loss, Optical Material, SHG, TTCS, Thermal Lens

1. Introduction

In recent days, the metal complexes of thiourea, allylthiourea and thiocyanate have emerged as strong second order nonlinear optical properties for laser application. The special interest has been focused on these materials due to their non-linearity, low cutoff and their ability to grow bulk crystals[1–3]. These materials have created a widespread impact on laser technology, optical communication etc. These materials have huge property of combining the high optical non-linearity and chemical flexibility of organic compounds with the mechanical properties and chemical inactivity of inorganic materials[4]. Thiourea molecule has the property to form widespread network of hydrogen bonds. When the thiourea molecules merge with inorganic salts the centrosymmetric nature of it becomes non-centro symmetric, which is essential for non-linear optical properties. Due to this instinctive attitude, changing the asymmetric conjugated organic molecules into inorganic distorted polyhedral, several thiourea complexes were synthesized and screened for their powder effeciencies and Tristhiourea Cadmium Sulphate (TTCS) was identified as one of the promising materials[5–10]. The absorption coefficient in the near IR region is very low and comparable with ZTS, so it can be used as a thermal lens in the area of IR detectors.

2. Experimental Procedure

2.1 Synthesis of TTCS and Solubility Measurement

The parental solution of the thiourea salt and cadmium sulphate was primed by dissolving the salt mixture in a Millipore water whose resistivity is 18.2 Mohmcm^{-1} in the ratio 1:3. Due to slow evaporation technique the solution is made to evaporate at room temperature which results in polycrystalline starting material according to the reaction

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

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The high purity of the salt is ensured by successive recrystallization process. As the growth and solubility are related to a greater extent, the solubility of the solute must be determined. For that the solute must be dissolved in the solvent i.e., in Millipore water in an airtight container maintained at constant temperature. Continuous stirring is done with the magnetic stirrer until the saturation is attained. The solubility data for various temperatures is found out to determine the level of saturation. To avoid decomposition care must be taken when the temperature reaches below 60^0C.

2.2 Seed Preparation

The recrystallized salt was dissolved in a Millipore water to obtain slightly under saturated solution. The solution is stirred continuously using a magnetic stirrer for 8 to10 hours at a room temperature. Then the solution is filtered twice using a Watt man filter paper. Seed crystals can be grown effectively by pouring the filtered solution in petri dishes. The petri dishes were covered by a porous paper in order to avoid dust and allows slow evaporation. The seed crystals were begin to grow after some days. From that grown crystals, very transparent and defect free crystals were taken to initiate the large size crystal growth.

2.3 Crystal Growth

The selected seeds were seasoned and then hung in the beaker containing the supersaturated solution. Large size crystals were grown by slow cooling technique. That is lowering the temperature 45^0c to room temperature at a rate of 0.1-to-0.2^{0}c. The good quality crystals were grown in a period of 50-60 days. Since TTCS crystal has lower solubility, the size of the crystal is limited. The grown crystal was shown in the (Figure 3).

3. Characterization Techniques

The TTCS sample was finely powdered and subjected to the powder diffraction analysis using a Rich-Seifert Diffractometer with CuKα (λ = 1.5418A) scanning over the range of 10-70^0 at a rate of 1^0 min^{-1} to record x-ray diffraction patterns. Single crystal XRD analysis of TTCS crystal was carried out using Bruker AXS, SMART single crystal diffractometer. The FTIR studies were taken out for freshly powdered sample of TTCS mixed with KBr and patellized with a hydraulic press in the range 400-4000 cm^{-1} with the help of Perkin-Elmer spectrometer. The amalgamation of sulphate in the crystal lattice and the presence of all functional groups were endorsed by FTIR spectrum. FTIR results were accompaniment by Laser Raman spectra recorded for the sample in the 100-3500 cm^{-1} using the excitation wavelength of 647.1 nm. The LCZ meter (model-chen Hua 1061) was used to find out the dielectric constant of the TTCS sample at low frequency region. The optical transmission spectra of the sample were logged in the range 200-1100 nm using Simadzu UV visible spectrophotometer. The NLO property of the powdered sample was studied using Nd-YAG laser of wavelength 1064 nm. The mechanical property of the grown crystal was found out by Micro hardness test using Leitz-Wetzlar hardness tester.

4. Results and Discussions

4.1 Crystal Growth and Morphology

The solubility of TTCS is found to increase with temperature (Figure 1). Due to lower solubility, the crystal size was limited and it is of the dimension 20*10*5 mm^3. Morphology of TTCS is found in (Figure 4). All the faces were indexed using goniometer observation single crystal x-ray diffractometer. The TTCS crystal system has 12 faces. In the morphology diagram bold characters are indicated the face in the upside of the crystal and italic characters represent the faces in the downs side of the crystal. {1-10},{-1-10},{-110},{-10-1},{010} are the prominent

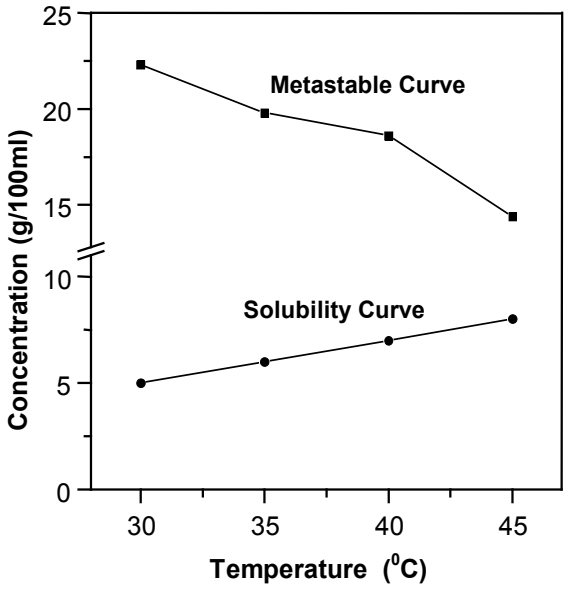

Figure 1. Solubility and metastable zone limit of TTCS.

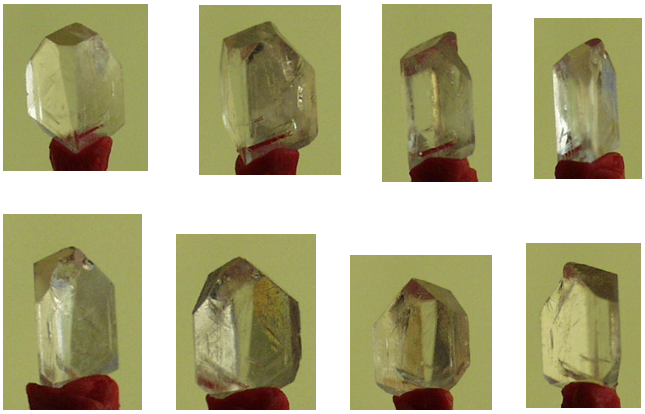

Figure 2. TTCS seed single crystals.

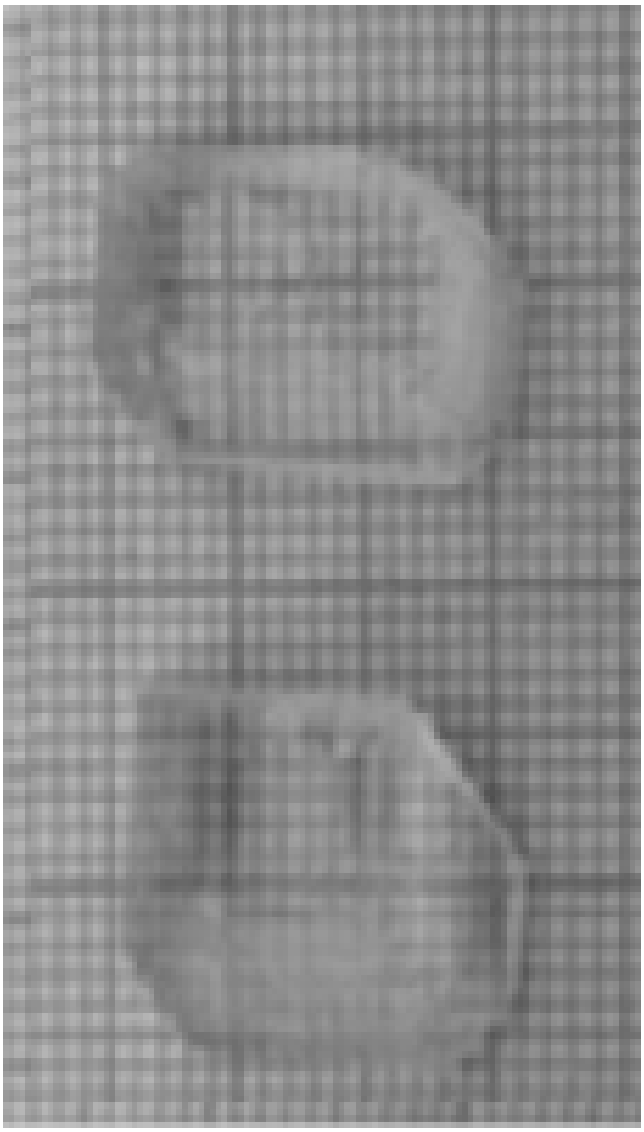

Figure 3. TTCS crystals.

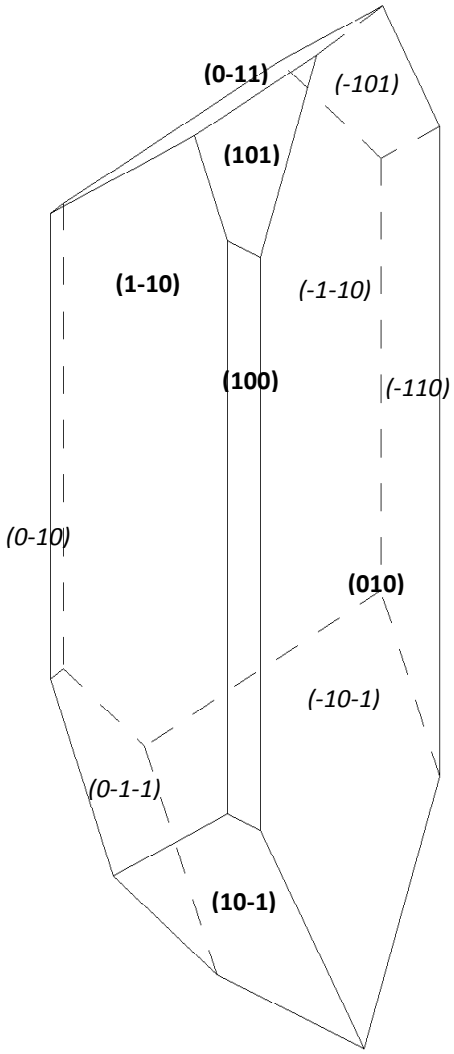

Figure 4. Morphology of TTCS (bold characters indicate the faces in the up-side of the crystal and italic characters represent the faces in the down-side).

faces, (0-100 and (010), (101) and –(101) are the parallel planes and {100},{0-11},{0-1-1},{101} are less prominent faces in the grown crystals. The relative importance in the crystal are (010)>(-1-10)>(1-10)>(-10-1)>(-110). (0-10)>(100)>(0-1-1)>(10-1)>(0-11)>(101)>(-101). The growth rate is faster along the [100] and [010] directions than along [001] direction.

4.2 XRD Studies

Powder x-ray diffraction studies confirm the triclinic structure of the TTCS crystal as shown in the Figure 5. The d spacing and the respective miller indices are shown in the Table 1. The experimental d values and the calculated d

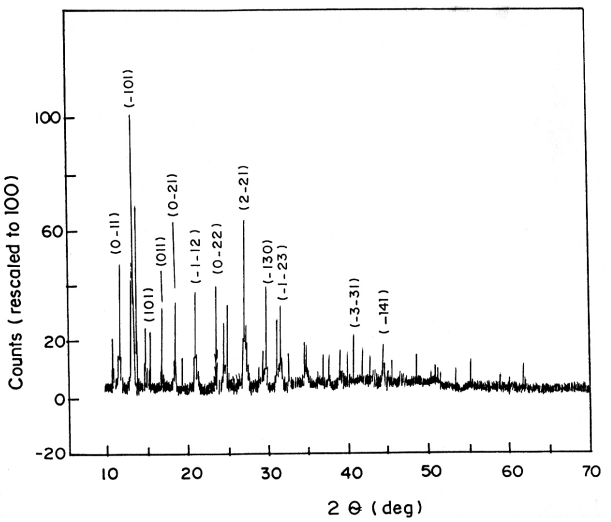

Figure 5. Powder X-ray diffraction of TTCS.

Table 1. SHG conversion efficiency of TTCS

Input power (mW)	Output power (mW)		Conversion efficiency (SHG) %	
	KDP	TTCS	KDP	TTCS
285	190	112	67	39
468	230	170	49	36
688	320	274	47	40
830	370	560	45	68

values were almost agreed with one another. The unit cell dimensions determined from single crystal x-ray diffraction analysis are a = 8.772A^0, b = 9.052A, c = 9.831A, V = 718.9A^3, α = 91.32^0, β = 111.91^0, γ = 95.52^0.

4.3 Thermal Analysis

The thermal stability of the grown crystal was studied using Thermos Gravimetric (TG) and Differential thermal Analysis. The analysis has been carried out using Seiko 6200 model analyzer in the nitrogen atmosphere. Dried powder sample of 15 mg of TTCS crystal was subjected to the analysis. The TGA and DTGA curve of TTCS is shown in Figure 6. It shows that the total weight loss of dried TTCS is about 50 percent. The grown TTCS crystal acquires thermal stability upto 220^{0}c and it starts to decompose above 220^{0}c.

4.4 Fourier Transform Infra-Red and Laser Raman Spectral Analysis

To record the FT-IR spectra of TTCS crystal, Perkin Elmer spectrometer was used in the range of 400-4000 cm^{-1} which

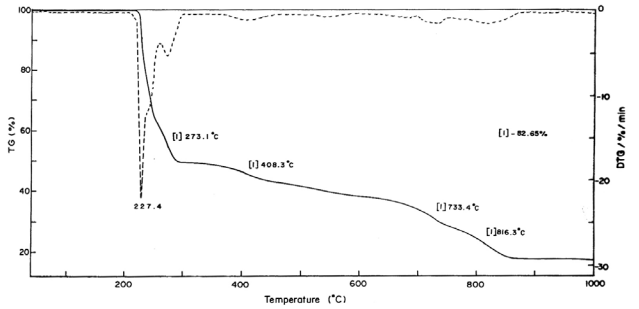

Figure 6. TGA and DTGA trace of TTCS.

was in the form solid dispersed KBr pellet. The recorded spectra was used to identify various functional groups. The laser Raman spectra was recorded with the help of dilzar Z-24 with excitation wavelength of 647.1 nm in the range 100-3500 cm^{-1} NH_2 group stretching vibration of thiourea and its metal complexes are the reason for the absorption band in the frequency region 2700-3500 cm^{-1} there is i.e., common band in FTIR and Raman spectra between 2700-3100 cm^{-1} due to NH_2 symmetric stretching vibration of NH_2 molecule. Asymmetric stretching vibration of NH_2 results in the peak appeared between 3200-3500 cm^{-1} which is found in both spectra. NH_2 asymmetric bending vibration gives rise to peak in FTIR spectrum around the region 1617 cm^{-1}. In laser Raman spectra the peak is found to be at1642 cm^1. N-C-N asymmetric stretching vibration of C=S occurs at 1470 in FTIR spectrum and it is at 1468 cm^{-1} asymmetric stretching vibration of thiourea. The medium intensity band at 710 cm^{-1} is due to N-c-N symmetric vibration in the FTIR spectrum the same appears very strongly in the Raman spectra at 711 cm^{-1} C=S asymmetric stretching vibration of thiourea assigns peak at 1403 and at 1408 in FTIR and Raman spectra. S-O asymmetric stretching vibration of SO_4 gives a band in the Raman spectra1 138 cm^{-1} S-O gives a band at 966 cm^{-1}. The same vibration corresponds to band at 1122 cm^{-1} and 968 cm^{-1} in the FTIR spectrum. The four fundamental frequencies are found at 1100,966,636 and 476 cm^{-1} in the laser Raman spectrum of TTCS crystal. Medium Intensity band found in the region 669 cm^{-1} is due to C=S symmetric stretching vibration. The peak at 227 cm^{-1} in the Raman spectrum with the strong intensity is due to Cd-S stretching vibration.

4.5 Dielectric Studies

An important characteristic property of a dielectric is its ability to support an electrostatic field while losing

Band assignments for TTCS FTIR spectra and Raman spectr a

Assignments	Wavenumbers for FTIR spectra	Wavenumbers for Raman spectra
NH_2 group stretching vibration of thiourea and its metal complexes	2700-3500 cm^{-1}	
NH_2 symmetric stretching vibration	2700-3100 cm^{-1}	2700-3100 cm^{-1}
NH_2 asymmetric stretching vibration	3200-3500 cm^{-1}	3200-3500 cm^{-1}
NH_2 asymmetric bending vibration	1617 cm^{-1}	1642 cm^{-1}
N-C-N asymmetric stretching vibration	1470 cm^{-1}	1468 cm^{-1}
C=S asymmetric stretching vibration of thiourea	1403 cm^{-1}	1408 cm^{-1}
S-O asymmetric stretching vibration of So_4	1122 cm^{-1}	1138 cm^{-1}
S-O symmetric stretching vibration of So_4	968 cm^{-1}	966 cm^{-1}
N-C-N symmetric vibration	710 cm^{-1}	711 cm^{-1}
Asymmetric bending vibrationof So_4	617 cm^{-1}	476 cm^{-1}
Symmetric bending vibration of So_4	476 cm^{-1}	484 cm^{-1}

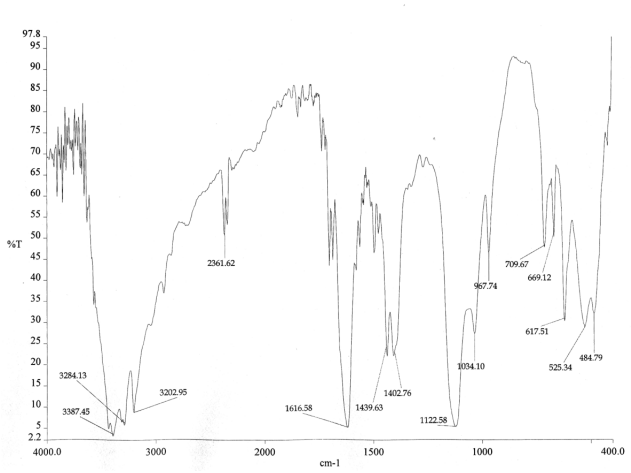

Figure 7. FTIR spectra of TTCS.

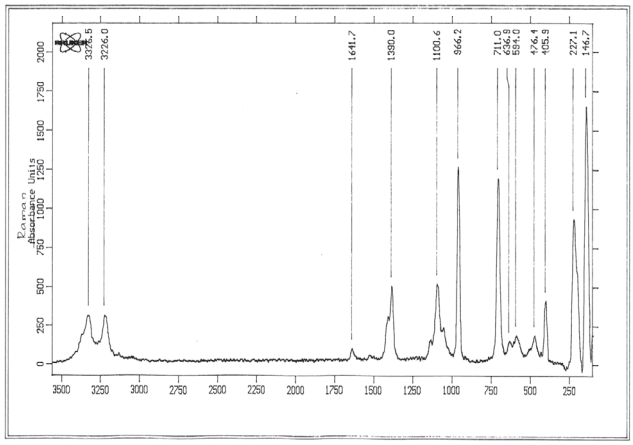

Figure 8. Laser Raman spectra of TTCS.

some energy in the form of heat. Dielectric study of NLO materials is very essential in the field of microelectronics for the operation of electro-optic devices which is based on Pockel's effect (ref). Figure 9 shows that the dielectric constant and dielectric loss are both inversely proportional to frequency. Increase in the value of dielectric constant at the lower frequencies contributed to space charge polarization. The lower value of dielectric loss reveals that there are fewer defects in the TTCS crystal.

4.6 Optical Transmittance Studies

The NLO crystals must have good optical transparency in the visible region in order to increase their application. UV visible spectra was recorded for the TTCS single crystals over the range 200-1100 nm. Figure 10 shows the uv-visible spectra of TTCS crystal with a transmission

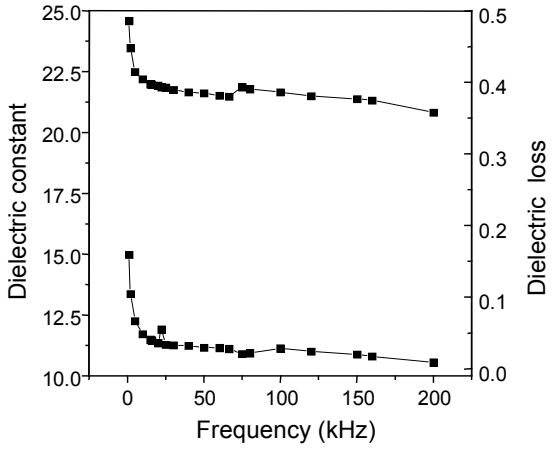

Figure 9. Variation of dielectric constant and loss factor with frequency for TTCS crystal.

Table 2. X-ray diffraction data of TTCS

2θ (◦)	d_{exp} (Å)	d_{cal} (Å)	Hkl
11.5	7.68	7.69	0-11
13.6	6.52	6.51	-101
14.2	6.23	6.24	110
16.0	5.53	5.54	101
17.1	5.20	5.19	011
17.7	5.02	5.01	0-21
19.2	4.61	4.62	020
20.0	4.45	4.44	200
20.8	4.28	4.27	-120
21.2	4.2	4.19	111
21.9	4.07	4.06	-1-12
23.2	3.84	3.83	0-22
24.3	3.67	3.66	1-12
25.2	3.54	3.53	021
26.1	3.42	3.41	1-22
26.7	3.35	3.34	-2-21
27.2	3.29	3.28	2-21
27.9	3.21	3.20	-112
29.6	3.03	3.02	-130
30.1	2.98	2.97	300
30.5	2.94	2.93	-221
31.9	2.82	2.81	0-23
32.3	2.78	2.72	-1-23
33.4	2.69	2.68	3-11
35.5	2.54	2.53	3-21
35.8	2.52	2.51	-1-33
37.0	2.43	2.43	103
38.6	2.33	2.33	040
39.9	2.26	2.26	2-23
41.0	2.20	2.20	-3-31
41.8	2.16	2.16	-411
42.7	2.19	2.12	0-14
43.7	2.07	2.07	-331
44.5	2.04	2.04	-141
45.4	1.99	1.99	023
49.5	1.84	1.84	-4-32
52.3	1.75	1.75	-413

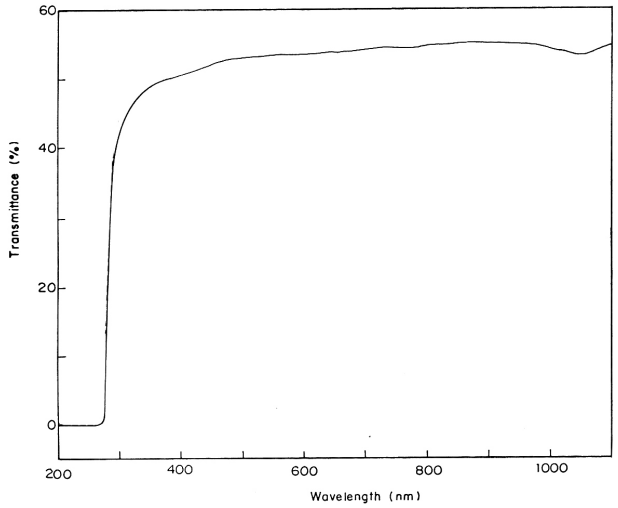

Figure 10. UV visible spectra of TTCS.

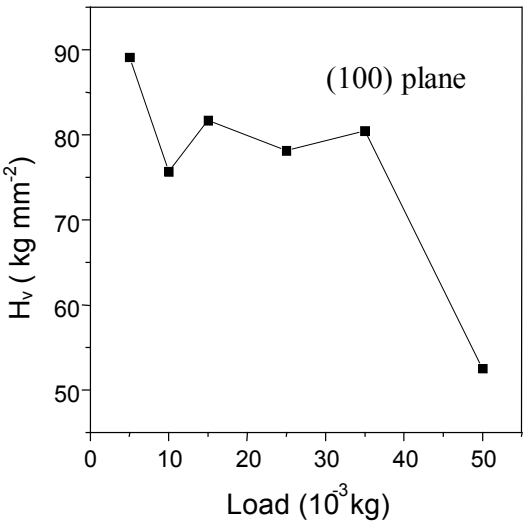

Figure 11. Vickers Hardness Number (VHN) of TTCS crystal.

confirming that crystal possess good optical transmission in the entire visible and IR region. Spectra also suggest that the grown crystal is suitable for second harmonic generation. Absorption at 250 nm in the uv range is due to electronic absorption by the thio-urea molecule.

4.7 Non-Linearoptical Studies

The NLO property of TTCS single crystal was confirmed by SHG efficiency test performed by Kurtz and Perry powder technique. Here the Nd-YAG laser which is operating at the wavelength of 1064 nm was made to

fall on the powdered sample packed in a capillary tube of diameter 0.154 mm. A green light emitted from the sample was detected by photodiode detector confirms the SHG efficiency of the grown crystal.

4.8 Vickers Microhardness Test

To evaluate the Hardness number several notches were made on the 010 face of the crystal. The Vickers Hardness number H_v has been calculated and d is the average diagonal of the notches in mm. The variation of the hardness H_v with load p is shown in Figure 11. The h variation ranges from 5 g to 50 g. For 5 g load the Hardness number is measured to be maximum value of 89.120 $kg.mm^{-2}$. Owing to the structural strain the hardness value becomes 75.71 $kg.mm^{-2}$ when the load is about 10 g. Attributing to the slip plane (010), again the load is increased the plane gets sheared so that the hardness number decreases with the formation of step in (010) plane. Now the load is increased to 15 g the hardness increases. For 25 g the hardness number decreases due to the shear taking place in that plane. Hence it is concluded that the (010) plane consists of slip planes.

5. Conclusion

The TTCS single crystal has been grown successfully by adopting slow evaporation and slow cooling techniques. The single crystal XRD and powder XRD pattern reveals that the crystal belongs to triclinic structure with space group's p-1. The presence of functional groups was confirmed by FTIR spectra. The coordination in the crystal occurs through sulphur was confirmed by Raman spectra. TTCS crystal has been found to be transparent from 200 to 1100 nm confirming their wide optical transmission range. TGA/DTA analysis showed the crystal possesses thermal stability up to 220^0c. Their low dielectric loss indicates that the crystal has fewer electrical defects. The nonlinear property of the crystal was confirmed by SHG test. These promising characteristic features of TTCS crystal proved it to be an attractive material for second harmonic generation.

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