Growth and Characterization of Tris Thiourea Calcium Sulphate (TTCS) Single Crystals

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ABSTRACT

Thiourea is potentially capable of forming coordinate bonds through both sulphur and nitrogen even though the extremely low basicity of the ligands militates against the formation of nitrogen metal bonds. Both these possibilities will be reflected in the infrared spectra of the complexes. The centrosymetric thiourea molecule when combined with inorganic salts yields non-centrosymmetric complexes, which has non linear optical properties. In the present study of Single crystals of pure Tris-thiourea calcium sulphate (TTCS) were grown by the slow evaporation solution growth method at a constant temperature. The qualitative analysis is study from the Fourier transform infrared spectroscopy, Single crystal rotational analysis and XRD method.

Key words: Solution growth TTCS, second harmonic generation(SHG),non linear optical(NLO) crystal, X-ray diffraction(XRD), Fourier transform IR spectroscopy(FTIR)

INTRODUCTION-Tris-thiourea calcium sulphate (TTCS) is a nonlinear optical (NLO) crystal .TTCS is prepared by reacting calsium sulfate and thiourea in a 1:3 molar ratio. It crystallizes in an orthorhombic crystal system with space group PCa21 and has the ability to withstand the thermal stress of a high power laser. It has a high laser damage threshold, low angular sensitivity and a wide spectral range of transparency.

It also has optical nonlinearity, excellent transmission and good mechanical strength as compared to many NLO materials. Due to the demand for reasonable crystal size, better NLO, thermal, mechanical, and optical properties in optoelectronic and SHG applications, continuous efforts are being made to modify the properties of ZTS crystal by adding different impurities and/or modifying growth parameters.

These were grown from aqueous solution by the low temperature solution growth (LTSG) method and by adopting the slow evaporation of solvent technique. These crystals were subjected to Fourier transform infrared (FT-IR) spectroscopy for measurement. It has a wide spectral range of transparency. These were grown from aqueous solution by the low temperature solution growth (LTSG) method and by adopting the slow evaporation of solvent technique. These crystals were subjected to Fourier transform infrared (FT-IR) spectroscopy, single crystal rotation method and XRD for measurement.

Method and preparation-Growth of TTCS from aqueous solution - The growth of Tris thiourea calcium sulphate crystals can be explained as follows:

The crystal grown using 99% pure chemical of Calcium sulphate and thiourea : for crystal growth, aqueous solutions of molecular proportion thiourea and calcium sulphate in the molar ratio of 3:1 were reacted under continuous stirring at room temperature (~36^0c) according to final reaction

$$CaSO_4 + 3CS(NH_2)_2 = Ca[CS(NH_2)_2]_3SO_4$$

The TTCS compound so obtained was dissolved to saturation in distilled water at room temperature and the solution was left in beaker.

For the growth process, pure grade chemical were used. The aqueous solution of calcium sulphate and thiourea were prepared in distilled water in the molecular ratio of 1:3. The calcium sulphate solution is added to thiourea solution, because of the same reason as maintained in above case. These solutions were reacted at room temperature with continuous stirring. The TTCS seed is grown by putting the solution in a peltry dish after 2 to 4 days later the nucleation process occur and seeds were obtained. Now in such bunch of seeds the good quality seed is selected and suspended in the supersaturated solution of TTCS. But due to low solubility of TTCS seed is grown is dissolves in the TTCS solution and also due to the wrong selection of method for TTCS crystal growth. It was unable to be grown to the large size single crystal but some measurement was taken.

X-ray diffraction by powder method-X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda=2d \sin\theta$). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range

of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacing allows identification of the mineral because each mineral has a set of unique d-spacing.

(a) Table 1 The following data collected for graph shown below

Position (θ)	d-spacing (Å)
18.1092	4.89465
22.9797	3.86708
25.5392	3.48503
28.6466	3.11366
29.4323	3.03231
31.4439	2.84275
32.0237	2.7926
34.1523	2.62325
36.365	2.46855
38.6981	2.32492
39.4402	2.28287
40.8776	2.20585
41.3835	2.18005
43.4157	2.0826
45.532	1.9906
46.8994	1.9357
47.5729	1.90985
48.7586	1.86615
49.2026	1.85034
50.8279	1.79492
52.3706	1.74562
54.422	1.68457
57.8465	1.64594
59.0529	1.59272
60.7414	1.56303
62.3202	1.52356
64.6193	1.4887
65.539	1.44117
67.0441	1.42316

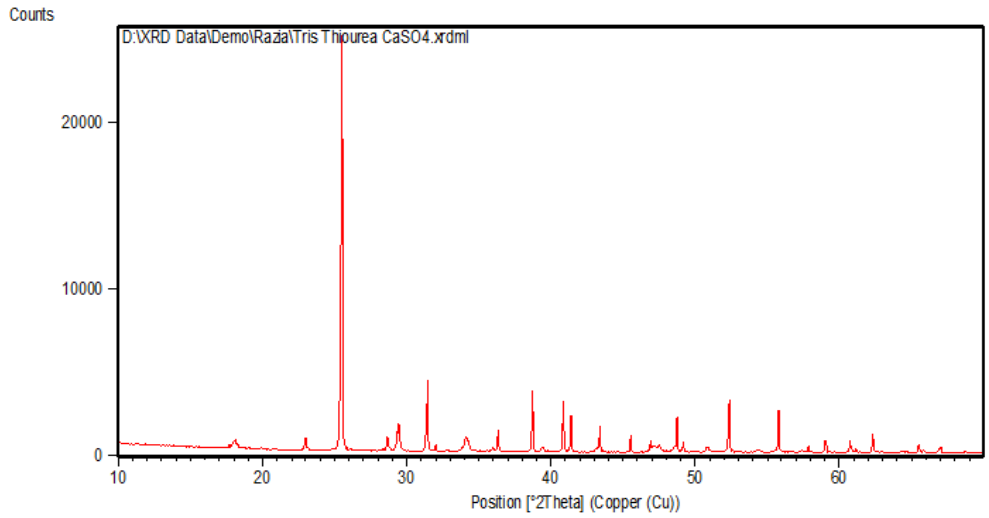

fig 1. Graph of TTCS for powder pattern

(b) **Single Crystal Rotation Method**: The most common experimental method of obtaining a detailed structure of a molecule, that allows resolution of individual atoms, single crystal X-ray diffraction (SXRD) is performed by analyzing the pattern of X-rays diffracted by an ordered array of many identical molecules (single crystal). When solidifying into the crystalline state, these individual molecules typically adapt one of only a few possible 3D orientations. When a monochromatic X-ray beam is passed through a single crystal, the radiation interacts with the electrons in the atoms, resulting in scattering of the radiation to produce a unique image pattern.

The data obtained from single crystal rotation is as below:

Crystal system: orthorhombic

Space group: Pnma

a/Å : 7.617(6)

b/Å: 8.511(6)

c/Å : 5.414(3)

Volume/Å : 3 351.0(4)

Z : 8

ρ (calc) mg/mm: 31.004

Fourier transform infrared ANALYSIS - The thiourea crystal exhibits the bands in the region 400-750cm^{-1},1050-1150cm^{-1}and 1300-1650cm^{-1}.These bands are arises due to the strong coupling between C=S,C-N and partial (NH_2) vibrations, respectively

TTCS the very strong vibrational lines observed at 590, 668cm^{-1} in FTIR spectrum are due to the C=S vibration modes. The strong peak at 2357 cm^{-1} have been assigned to C≡N stretching vibrational modes.

(c) Table 2 The following data collected for graph shown below

Wavenumber(cm^{-1})		Assignment
Thiourea	TTCS	-
469		**symmetric NCS bending**
	590	**C=S vibrations**
	668	**C=S vibrations**
740		**C=S symmetric stretching vibration mode**
	871	**C-H bending**
1089		**C=N symmetric stretching vibration mode, S=O stretching vibrations(sulfoxides)**
1417		**C=S asymmetric stretching vibration mode, Sulfites**
1627		**N-H bending vibrations,-N=N- stretching vibrations**
	2357	**C≡N stretching vibrations**
3100-3300		**Imines(=N-H); one band**

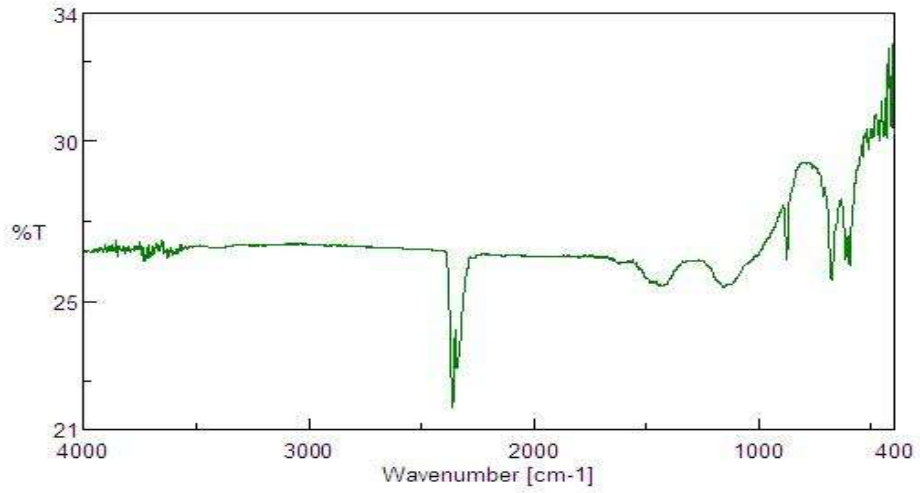

FIG 2. Ftir graph for TTCS

RESULT-We obtained seeds, but large size single crystal were not grown; Because of wrong selection of crystal growth techniques for this substance whose solubility is very low in the water. The measured lattice parameters obtained from single crystal rotation analysis is a = 7.617 Å,b = 8.511 Å, c = 5.414 Å,ρ = 3 1.004 calcmg/mm. The measured interplanar 'd' spacing for different position of angles from the powder pattern x-ray diffraction were analyzed. The FTIR studies revealed the strong peak at 2357 cm^{-1} have been assigned to C≡N stretching vibrational modes.