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XRD, SHG, HARDNESS, FTIR AND SEM STUDIES OF THIOUREA CRYSTALS DOPED WITH SODIUM CHLORIDE

A. Prabumarachen*, S. Ramalingom* & T. Chithambarathanu**
* Department of Physics, Vivekananda College, Agasteeswaram, Tamilnadu
** Department of Physics and Research Centre, S.T Hindu College, Nagercoil, Tamilnadu

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Abstract:

Thiourea crystal is sulphur containing nonlinear optical (NLO) material and it has a lot of applications in opto-electronics and laser technology. The properties of thiourea may be altered by adding organic and inorganic dopants into the interstitial positions of thiourea. In this work an inorganic material viz., sodium chloride is added into thiourea to change its physical and chemical properties. Single crystals of sodium chloride doped thiourea were grown by solution method at room temperature. Different concentrations of sodium chloride were added into the host thiourea crystal and hence the morphology of the crystals has been modified. The grown crystals were subjected various studies like XRD studies, SEM studies, FTIR studies, SHG studies and hardness studies to find the various properties and the obtained results are discussed.

Key Words: Thiourea, Doping, Single Crystal, Crystal Growth, Characterization, XRD, Hardness, SEM, SHG & FTIR

1. Introduction:

Nonlinear Optical (NLO) materials have potential applications in Second Harmonic Generation (SHG), optical storage, optical communication, photonics and they are attracting a great deal of attention because of their use in optical devices, such as optical switches, optical modulators, optical bi-stable devices, electro-optical devices, etc. [1, 2]. NLO materials can be classified into organic, inorganic and semiorganic materials. Organic materials have been of particular interest because the nonlinear optical responses in this broad class of materials are microscopic in origin, offering an opportunity to use theoretical modeling coupled with synthetic flexibility to design and produce novel materials. Also, organic NLO materials are attracting a great deal of attention as they have large optical susceptibilities, inherent ultrafast response times and high optical thresholds for laser power compared with inorganic materials [3-6]. Thiourea is an interesting organic NLO material and is an organosulfur compound with the formula $SC(NH_2)_2$. It is structurally similar to urea, except that the oxygen atom is replaced by a sulfur atom, but the properties of urea and thiourea differ significantly and it is used in textile processing. Thiourea is an organic material and it can combine with organic and inorganic materials to form many thiourea complexes [7-10]. More than 700 structures of metal thiourea complexes were reported by Cambridge structural database [11]. Spectroscopic and microscopic studies of thiourea single crystals were performed and reported by Patel *et al*. [12]. Thiourea crystals exhibit pyroelectric effect which is utilized in infrared Scanning electron microscopy detection and infrared imaging [13]. To improve the various physical and chemical properties of thiourea crystals, sodium chloride was added as the dopant in this work. The aim of the work is to grow undoped and sodium chloride doped thiourea crystals and to subject the grown crystals to different characterization studies for analyzing the properties.

2. Solubility Curve of Thiourea:

Analytical reagent grade thiourea and deionised water (solvent) were used in the present crystallization experiment. The solubility of thiourea was determined separately for different temperatures viz., 30, 35, 40, 45 and 60°C. The measurement was performed by dissolving pure thiourea in deionised water in an airtight container with constant stirring using magnetic stirrer. After achieved saturation the equilibrium concentration of thiourea was determined gravimetrically. The solubility curve for different temperatures is presented in Figure 1. It is observed that the solubility increases linearly with increase of temperature and the sample show positive temperature coefficient of solubility. The solubility data could be used to prepare saturated and supersaturated solutions at a particular temperature and these solutions can be used for growing doped and undoped crystals of thiourea.

3. Preparation of Sample Crystals:

3.1 Crystal Growth: Analar reagent grade thiourea, sodium chloride and de ionised water were used in the present investigation. 400 ml of deionised water was taken in a 500 ml beaker. Using the known solubility data, recrystallised salts of thiourea was added and stirred well with a magnetic stirrer to attain saturation. The solution was filtered using Whatman filter paper and distributed equally (100 ml) in the growth vessels. Sodium chloride of 1 M.%, 2 M.%, 3 M% were added in three crystallizers and the remaining one containing the mother solution was used as a standard. The solution was stirred well till the complete dissolution of sodium chloride. The solutions were once again filtered. The pH of the solution was found to be 8.5. The crystallizers were closed with perforated polythene papers and kept at a constant temperature 30°C. As the solvent evaporates slowly, the solution get supersaturated and the nucleation starts and hence the crystal grows. Within a period of 20-25 days, pure and sodium chloride doped thiourea crystals were harvested and the grown crystals are shown in the figure 2.

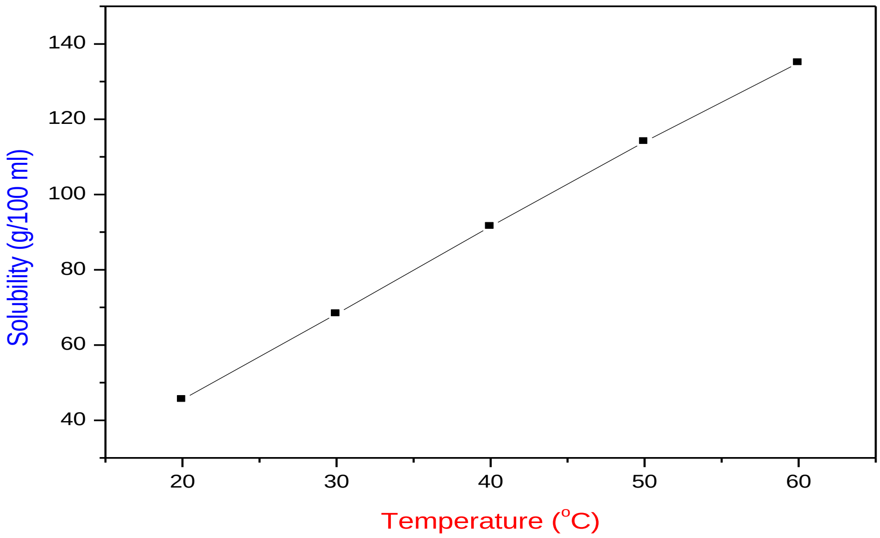

Figure 1: Variation of solubility with temperature for thiourea

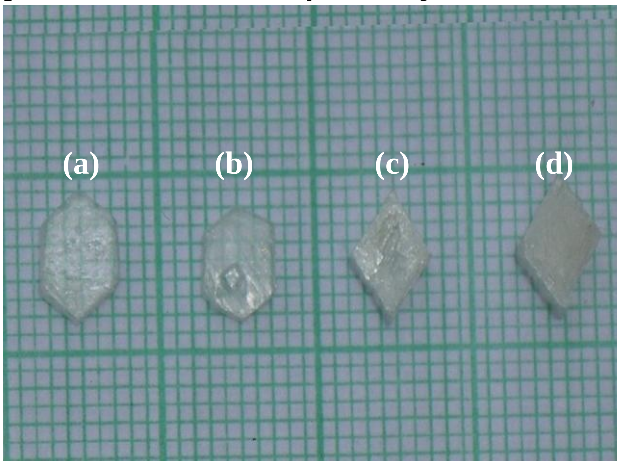

Figure 2: Grown crystals of (a) undoped and (b, c, d) sodium chloride doped thiourea crystals

3.2 The effect of Dopants and Morphology: It was observed that the growth rate and hence the habit of the crystal mainly depend on the pH and the dopant concentration present in the mother solution. From the figure 2, it is observed that increase in sodium chloride concentration changes the crystal habit and the morphology of the thiourea crystals changes as the concentration is varied. The morphology of the growing crystal is determined by the growth rates in different crystallographic directions If the growth rate is uniform, the distance from the centre of the crystal to the different crystal faces are proportional the relative growth rate of the crystal faces. Under certain suitable conditions fast growing as well as slow growing faces disappear. If the growth rate is uniform in a direction perpendicular to a certain face, then that face grows larger in size [14, 15]. The presence of sodium chloride dopant in the mother solution induced varying growth rates in different faces. Sodium chloride gets adsorbed in the crystal lattice, leading to the variation in the growth rates. Hence the hexagonal morphology disappears. The habit of the pure thiourea single crystal changes from hexagonal to tetragonal when doped with sodium chloride.

4. XRD Studies:

Powder X-ray diffraction analysis using CuK_{α} radiation of wavelength 1.54056Å X-ray diffractometer (Model Ritz-170) was carried out and CELN software package was used to index the various peaks. The X- ray powder diffraction pattern of the sodium chloride doped thiourea is presented in Figure 3. The lattice parameters were presented in table 1. For the comparison, the lattice parameters of undoped thiourea crystal are also given in the table. It is confirmed that both undoped and sodium chloride doped thiourea have the orthorhombic structure.

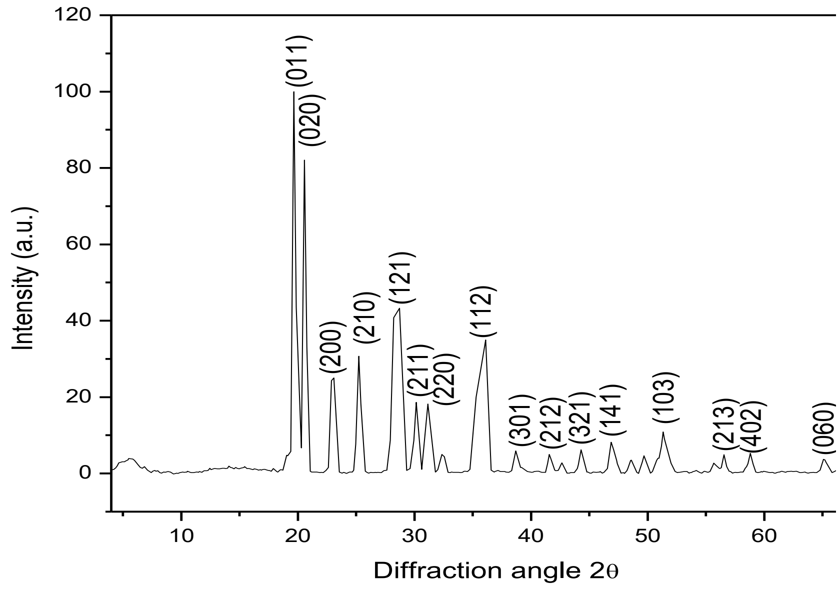

Figure 3: X- ray powder diffraction pattern of the sodium chloride doped thiourea

Table 1: X-ray diffraction data for undoped and NaCl doped thiourea

$\alpha = 90^o$, $\beta = 90^o$ and $\gamma = 90^o$

	a Å	b Å	c Å	Unit cell volume $(Å)^3$
Undoped thiourea	7.657	8.588	5.485	360.68
NaCl doped thiourea	7.658	8.600	5.515	363.27

5. FTIR Studies for Sodium Chloride Doped Thiourea Single Crystal:

The Fourier Transform infrared (FTIR) spectrum of the grown the sodium chloride doped thiourea single crystal was recorded using JASCO FTIR 460 spectrometer by KBr pellet technique in the range 450-2500 $cm^{-1}$and it is shown in the figure 4. The observed bands were assigned and presented in Table 2. The change in vibrational frequencies for the NaCl doped thiourea may be due to the presence of the dopant. For the comparison purpose, the FTIR assignments for undoped thiourea are also given in the table 2 [16].

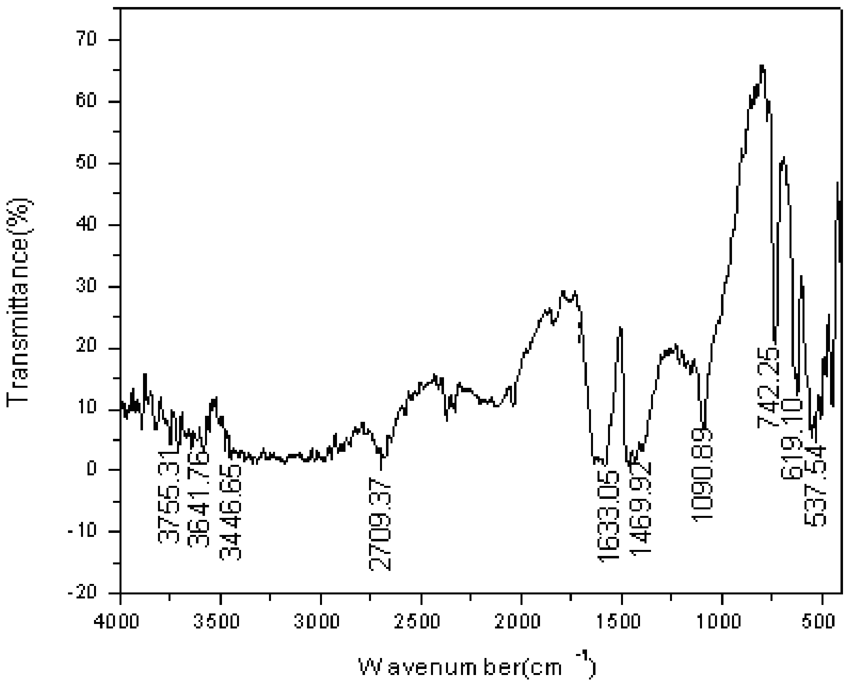

Figure 4: FTIR spectrum for NaCl doped thiourea

Table 2: Vibrational assignments for NaCl doped thiourea

Wave number (cm^{-1}) Thiourea	**Wave number (cm^{-1}) NaCl doped Thiourea**	**Assignments**
494	537.54	(N-C-N) Asymmetric stretch
740	619.10	(C=S) stretching
1089	742.25	(C-N) stretching
1417	1090.89	(C=S) Asymmetric stretching
1470	1469.92	(N-C-N) Symmetric stretching
1627	1633.05	(NH_2) scissors
3500-3400	3500-3400	NH_s stretching

6. Thermal Analysis:

Thermo gravimetric and differential thermal analysis was carried out using an SDTQ 600 U8.3 thermal analyzer in the temperature range 30-1100° C. The temperature and rate at which materials undergo physical and chemical transitions during heating and cooling and the energy and weight changes associated with the temperature is the subject matter of thermal analysis [17, 18]. The thermo gravimetric and differential thermal analysis was carried out for sodium chloride doped thiourea single crystal and the recorded thermal curves are shown in Fig.5. From the TG curve, it is observed that there is no weight loss up to 100°C. This indicates that there is no water molecule in the sample and the sample hass the thermal stability (87.72% wt loss) up to 183.76°C. It is observed that there is a sharp endotherm at 242.85°C. This endotherm is due to the decomposition of the compound. Only 22.22% weight loss is observed as the residue.

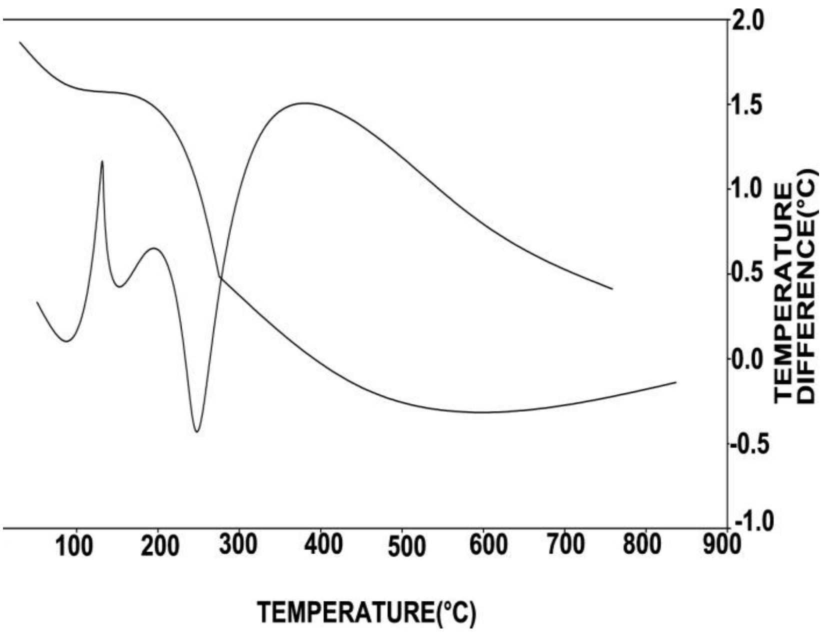

Figure 5: TG/DTA curves sodium chloride doped thiourea crystal

7. Measurement of SHG:

The powder Second harmonic generation (SHG) test confirms the NLO property of pure and doped thiourea crystals. The SHG test was carried out by the powder technique of Kurtz and Perry [19] using Nd:YAG laser with first harmonics output of 1064 nm, width 8 ns and repetition rate 10 Hz. The measured values of SHG for undoped and sodium chloride doped thiourea crystals are provided in the table 3. Thiourea is an organic molecular compound which crystallizes in non-centrosymmetric space group and this gives SHG. When thiourea is doped with sodium chloride, it is observed that the SHG efficiency relative to that of KDP increases with increase in sodium chloride dopant concentration. This shows that doped thiourea crystals will be better materials for NLO applications. Due to the presence of sodium chloride in thiourea crystal lattice, there is an increase in polarizability of the moleculea, which tends to increase the SHG efficiency.

Table 3: Values of SHG for undoped and sodium chloride doped thiourea

Sample	SHG conversion efficiency
Thiourea crystal	0.73
Thiourea + 1 M % of Sodium chloride	1.65
Thiourea + 2 M % of Sodium chloride	1.67
Thiourea + 3 M % of Sodium chloride	1.71

8. SEM Studies:

SEM studies were carried out for the grown crystals and the surface features of a crystal is a key to understand the mechanism and history of crystal growth. The surface studies also provides information about the nature and distribution of imperfections in a crystal. Figs. 6 and 7 represent the SEM micrographs of the undoped and sodium chloride doped thiourea crystals. Well defined growth layers with large step growth was observed in thiourea crystal. The growth layers observed on the surface is produced by secondary nucleations and spreading of layers from its growth centers. The SEM micrograph of the sodium chloride doped thiourea shows that the surface is smooth and the relatively planes reveal the perfection of the crystal.

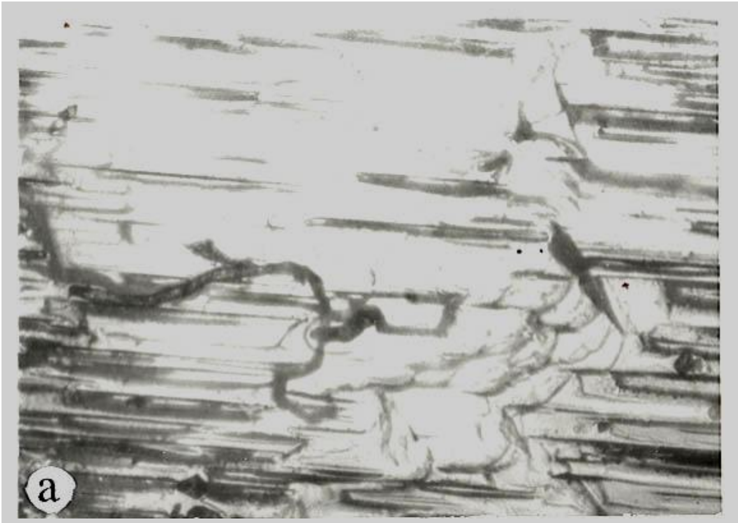

Figure 6: SEM microphotograph undoped thiourea crystal

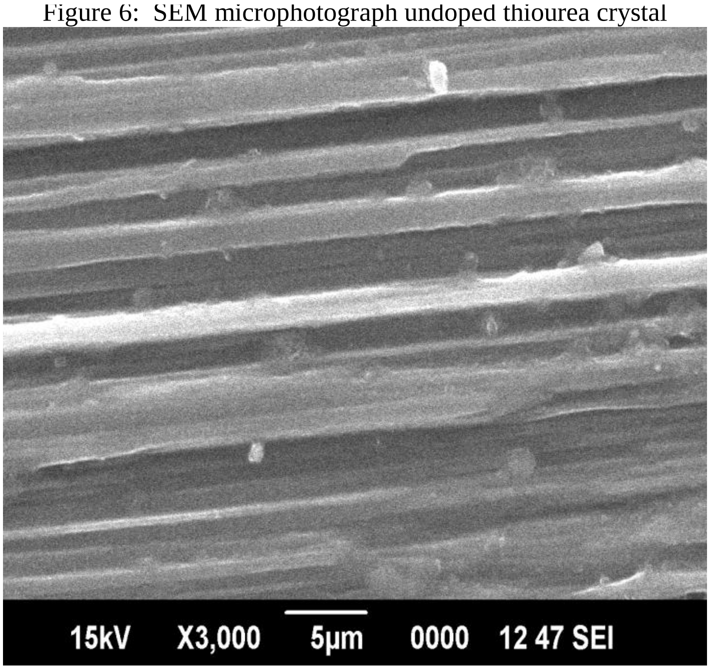

Figure 7: SEM microphotograph sodium chloride doped thiourea crystal

9. Hardness Studies:

Hardness can be defined as macro, micro and nano according to the forces applied and displacement obtained. Among the various methods of hardness measurements, static indentation test is the popular and simplest, in which a steady load is applied to an indenter. The indenter may be a ball or diamond cone or diamond pyramid. The hardness is calculated from the area or the depth of indentation produced. The indenter is made up of a very hard material to prevent its deformation by the test piece, so that it can cover materials over a wide range of hardness. By definition the indentation hardness is the ratio of the applied load to the surface area generated due to indentation. Whenever mixed and doped crystals are used, hardness is of prime importance because the hardness of mixed and doped crystals always exceeds the microhardness of the individual constituent materials. Microhardness studies are carried out to understand the mechanical properties of the crystals. For this reason either a hardened steel sphere or a cone diamond pyramid is employed. In general, pyramidal indenter is preferred to obtain geometrically similar impression for various loads. In the Vickers hardness test, an indenter with a square based pyramid is used for which the angle between opposite faces is ideally 136º. From the general definition of hardness, for a given diagonal *d* mm of the square impression formed on the sample and for the load *P*,

$$\text{Vickers hardness value, Hv} = \frac{2P\sin(\alpha/2)}{d^2}$$

$$\text{Since } \alpha = 136\,^{\circ},\ H_v = \frac{1.8544P}{d^2}\,kg/mm^2$$

Here P is the applied load in kg and d is the diagonal length of the indented impression in mm [20-23]. The Vickers hardness values of the samples have been measured using a Vickers microhardenss tester and the obtained values for undoped and sodium chloride doped thiourea crystals are given in the tables 4 and 5. From the results it is observed that hardness number increases as the load increases for the samples. Hardness number is found to be increasing when thiourea crystals are doped with sodium chloride and the hardness with load is primarily caused by the work hardening surface layers. The increase of hardness number for the doped crystal is may be due to the presence of dopants in crystal lattice.

Table 4: The calculated values of microhardness for thiourea crystal

S.No	Load (g)	H_v ($kgmm^{-2}$)
1	10	21.53
2.	20	51.62
3.	30	77.32
4.	40	98.4.01
5.	50	111.45

Table 5: Calculated values of microhardness for NaCl doped thiourea crystal

S.No	Load (g)	H_v ($kgmm^{-2}$)
1	10	25.78
2.	20	58.62
3.	30	83.32
4.	40	100.01
5.	50	128.85

10. Conclusions:

Single crystals of undoped and sodium chloride doped thiourea crystals were grown by solution method with slow evaporation technique. There are the morphological changes occured when thiourea crystals were doped with sodium chloride. Solubility was found to be increasing with increase of temperature for thiourea crystal. The crystal sturucture of the grown crystals of sodium chloride doped thiourea is observed to be orthorhombic. The SHG value of thiourea crystal has been enhanced when it is doped with sodium chloride. The various functional groups of the samples have been found by FTIR spectral stuides. SEM studies reveal the surface features of the samples. The thiourea crystals are hardened when they are doped with sodium chloride.

11. Acknowledgement:

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