

Growth, Spectroscopic, Mechanical and Dielectric Properties of Picric Acid doped Thiourea Single Crystals

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Abstract: Single crystals of pure and picric acid doped thiourea were grown by slow evaporation technique. Single crystal structure was determined by X-ray diffraction data and it reveals that the crystal belongs to orthorhombic crystal system with space group of Pnma. The dielectric constant and dielectric loss were calculated by varying frequencies at different temperatures. The microhardness test reveals that the crystals possess very good mechanical strength. Vibration spectrum reveals the symmetries of molecular vibrations.

Keywords: slow evaporation technique, dielectric studies, mechanical strength etc,

I. Introduction

Single crystals of thiourea are being used broadly in the electronic industry as polarization filter, electronic light shutter, electronic modulator, optical voltmeter and as elements of electro-optic and electro-acoustic devices. Thiourea crystals exhibit pyroelectric effect, which is utilized in infrared (IR), ultraviolet (UV), scanning electron microscopy (SEM) detection and infrared imaging (1). The search for new advanced materials is an important area of contemporary research in numerous disciplines of science and the development of many new technologies. Organic crystals are made of highly polarizable molecules, the so-called conjugated molecules, where highly delocalized p-electrons can easily move between electron donor and electron acceptor groups on opposite sides of the molecule, inducing a molecular charge transfer and the molecules are adequately packed to build up a non-centrosymmetrical crystal structure that provides non-vanishing second-order non-linear coefficients [2,3]. The salts between organic molecules and dicarboxylic acids have been reported by many authors [4–7]. In the present study the growth of picric acid doped thiourea single crystals and its characterization such as solubility, XRD, FTIR, dielectric studies and micro hardness are discussed.

1.1. Synthesis

Recrystallised salts of (analar reagent grade) thiourea, (NH_2CSNH_2), picric acid and de-ionized water were used in the present crystal growth experiment. Saturated aqueous solutions were prepared at room temperature following the known solubility data. The solubility of thiourea in de-ionized water (100ml) at room temperatures was 68gm. Saturated solution of thiourea of 400ml at room temperature (29°C) was prepared using recrystallized salts of thiourea and de-ionized water were stirred well using a magnetic stirrer. Picric acid of 0.5mol% and 1mol% were added in two beakers of mother solution (200ml) and the remaining solution was used as standard. The solutions are mixed for about 5 hours using a magnetic stirrer with 500rpm to ensure homogeneous temperature and concentration through out the volume of the solution. The pH value of the solution is found to be 7. The saturated solutions were filtered with whatmann filter paper and then covered with perforated transparent polythene paper and left undisturbed for slow evaporation. The solvent evaporates slowly leading to supersaturation which in turn initiates nucleation and the crystal grows. Good quality single crystals were grown in 21 days.



Figure 1. Thiourea 0.5mol% picric acid doped thiourea 1mol% picric acid doped thiourea

1.2 Solubility

In solution growth technique the size of a crystal depends on the quantity of the material available in the solution which is decided by the solubility of the material in that solvent. The solubility of the synthesized material was determined by adding water maintained at constant temperature to a known quantity of the material till the material was completely dissolved. Using this technique, we evaluate the magnitude of the solubility of thiourea single crystals and 0.5 and 1 mol% picric acid doped thiourea single crystals at various temperatures between 25°C and 50°C which is shown in fig 2. The grown crystals have a positive temperature coefficient of solubility. Thus slow cooling of aqueous solution of pure and picric acid doped thiourea crystal could be attempted to grow bulk crystals [8].

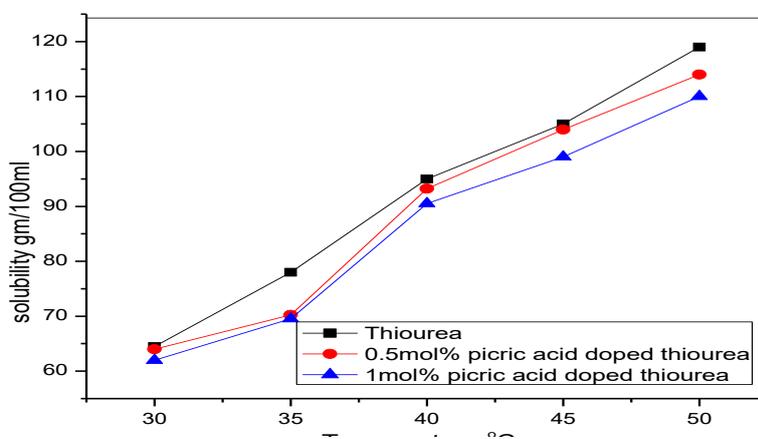


Figure 2. Solubility curve

1.3. Analyzing techniques

The grown crystals were confirmed by single crystal X-ray diffraction analysis using ENRAF NONIUS CAD4 diffractometer. Powder X-ray diffraction (XRD) was recorded using XPERT PRO diffractometer with CuK α radiation ($\lambda=1.5405 \text{ \AA}$). The crystals were characterized by SPECTRUM ONE CPU 32 spectrophotometer, using KBr pellet technique. The dielectric study on thiourea single crystals was carried out using the instrument, HIOKI3532-50 LCR HITESTER. The microhardness measurement of the crystals was carried out by a REICHERT MD 4000E ultra microhardness tester with a diamond pyramidal indenter.

II. Results And Discussion

2.1. Single crystal diffraction

Single crystal x-ray diffraction analysis for the grown crystals is carried out to confirm the crystalline nature and also to identify the unit cell parameters using ENRAF Nonius CAD4 single crystal X-ray diffractometer. It is observed that thiourea crystals crystallize in the orthorhombic system with lattice primitive and space group Pnma. The lattice parameters are tabulated below:

Table 1: Lattice Parameters of pure and Thiourea doped picric acid

Lattice parameters	Thiourea	0.5mol% picric acid doped thiourea	1mol% picric acid doped thiourea
a(\AA)	7.481	7.493	7.497
b(\AA)	8.535	8.553	8.555
c(\AA)	5.472	5.480	5.481
V(\AA^3)	349.389	351.200	351.533
$\alpha=\beta=\gamma=90^\circ$			

2.2. Powder X-ray Diffraction

The grown single crystals of pure and picric acid doped thiourea are subjected to powder X-ray diffraction. The powder form of the above mentioned crystal is taken for the analysis using XPERT PRO diffractometer. The positions of the peaks are found to be in good harmony with the data available in JCPDS files and are presented in fig 3. In the case of 0.5 mol% picric acid doped thiourea crystals, no new peaks are detected, rather a slight shift in the position of some peaks is observed. The sharp intense peaks on the patterns reveal that the crystallites are pure and dislocation free.

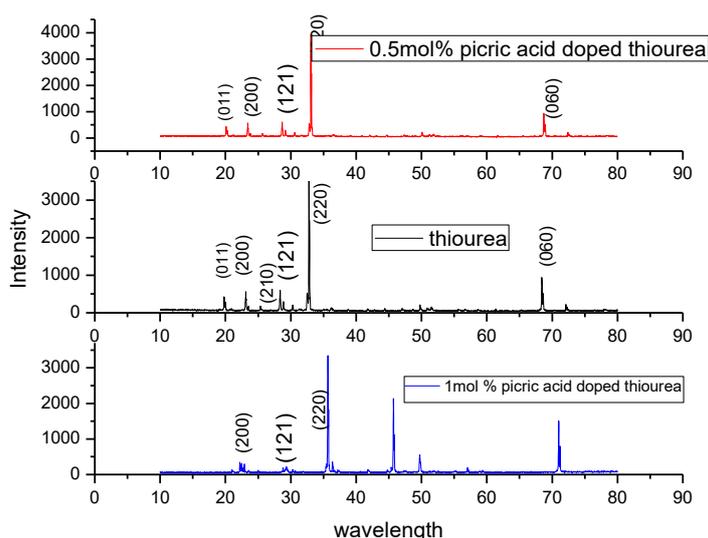


Figure 3. The Powder XRD pattern

2.3. FTIR analysis

The FTIR spectral analysis (fig 4) for the grown crystals is recorded in the range of 400-4000cm⁻¹ using SPECTRUMONE, CPU 32 spectrophotometer using the KBr pellet technique. The H₂O twisted is occurred at 501 cm⁻¹. The symmetric and asymmetric C=S stretching vibrations of thiourea are observed at 729 cm⁻¹. The COH stretching mode occurred at 1083 cm⁻¹ in the spectrum. The CH₃ asymmetrical deformation, or CH₂ bending vibration or N-C-N asymmetric stretching mode is assigned at 1415 cm⁻¹. The =CH valence and ≡CH valence of thiourea are observed at 3161 cm⁻¹ and 3325 cm⁻¹ respectively. The ≡CH symmetrical band is assigned at 3373 cm⁻¹ in the spectrum. The symmetric NH₂ stretching is assigned to the band at 3790 cm⁻¹.

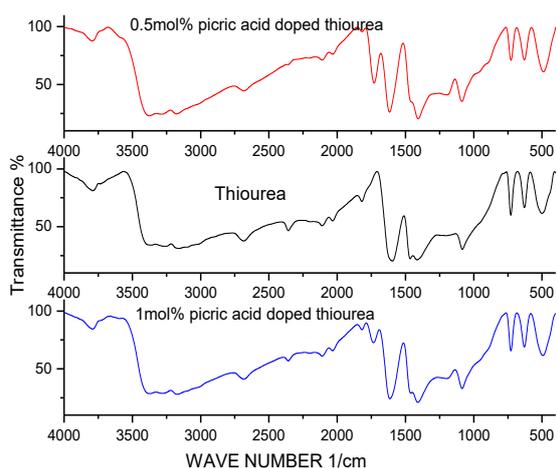


Figure 4. The FTIR spectrum

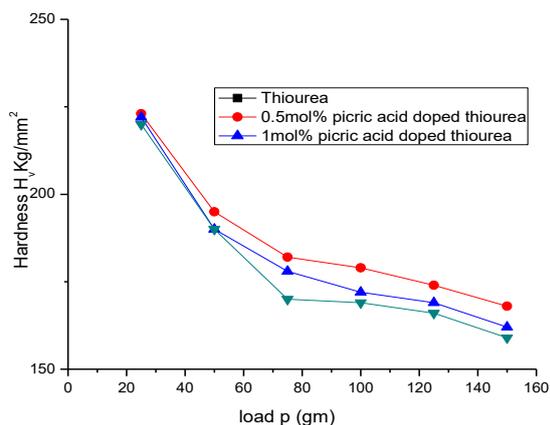


Figure 5. The load vs hardness number

2.4. Microhardness Studies

Microhardness measurements were made using a Leitzmicrohardness tester fitted with a diamond pyramidal indenter. The applied load is varied from 25 to 150 g for a constant indentation period of 10s. The Vicker's hardness number Hv is calculated using the relation

$$Hv = 1.8544P/d^2 \text{ Kg/mm}^2$$

where P is the indenter load in kg and d is the diagonal length of the impression in mm[9]. The variation of Hv with applied load is shown in Fig5. It is evident from the plot that the microhardness of the crystal decreases with increasing load. For loads above 150g cracks developed on the surface of the crystal and are due to the release of internal stress generated locally by indentation.

2.5. Dielectric Studies

The dielectric constant is one of the basic electrical properties of solids. The dielectric constant is the measure of how easily a material is polarized in an external electric field [10]. Dielectric property of the crystal is correlated with electro-optic property of the crystals [11]. The dielectric study of the grown crystal is carried out using the instrument, HIOKI3532-50 LCR HITESTER. The capacitance is measured in the frequency range of 100Hz to 5MHz. The dielectric constant is calculated using the relation $\epsilon_r = Cd/A \epsilon_0$ and is shown in fig6.

The larger value of dielectric constant at lower frequency is due to the impedance of the motion of charge carriers at the electrodes. This result space charge and macroscopic distortion [12]. The dielectric constant is low at higher frequencies and is due to the fact that at higher frequencies the ionic and electronic polarizations are active [13]. According to Miller rule, the lower values of dielectric constant are a suitable parameter for the enhancement of SHG coefficient [14]. The dielectric loss versus log frequency is shown in fig 7. The dielectric loss values are found to be large at low frequencies and low at high frequencies. The low dielectric loss at higher frequency of the sample indicates that the crystals possess lesser number of electrically active defects [15]

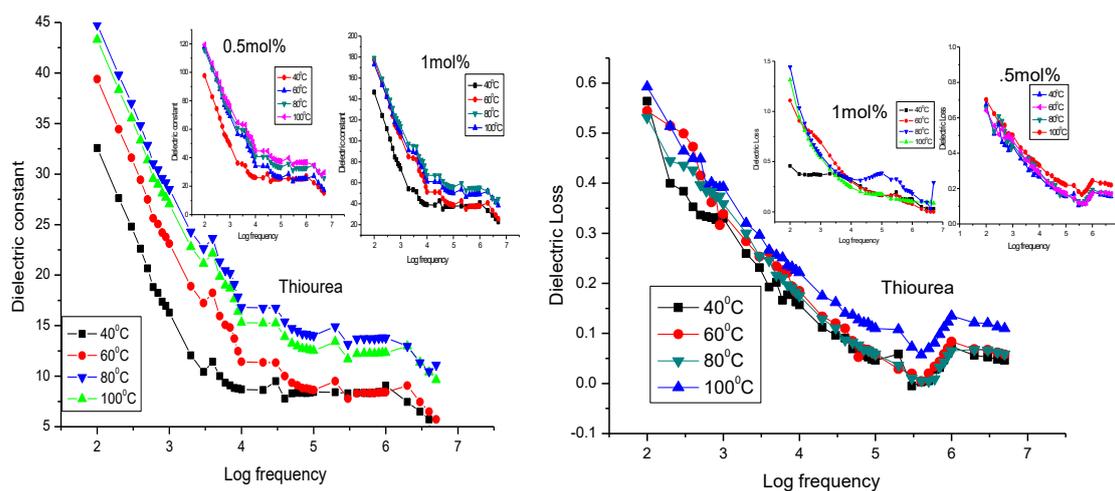


Figure 6. Log frequency vs dielectric constant **Figure 7.** Log frequency vs dielectric loss

III. Conclusion

Pure and picric acid doped thiourea single crystals were grown by slow evaporation method. The grown crystals were characterized using single crystal X-ray diffraction analysis, which shows that thiourea belong to orthorhombic system. The presence of functional groups thiourea and the bond interaction have been confirmed by FTIR analysis. Low dielectric constant and dielectric loss at high frequency suggest that the sample possesses enhanced optical quality with lesser defects. From the mechanical measurements, it was observed that the hardness decreases with increase of load. Hence it is concluded that good quality pure and picric acid doped thiourea single crystals with good thermal and mechanical stability can be grown by slow evaporation technique and is suitable for the fabrication of various optoelectronic devices.

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