Investigation on the growth and characterization of sulphuric acid and nitric acid doped thiourea single crystals

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Sulphuric acid and nitric acid doped thiourea single crystals were grown by solvent evaporation technique. Four distinct morphologies of thiourea crystals were observed in the growth cells. The structures of the crystals are identified as orthorhombic by single crystal X-ray diffraction technique. The spectral bands and optical transmission spectrum of the grown crystals have been compared with similar thiourea complexes using FTIR spectrum in the range 400 – 4000 cm^{-1} and UV-Vis spectrometer respectively. The mechanical hardness is performed on the grown crystals by Vicker's microhardness study and the results reveal that the crystals are mechanically moderately soft. The stiffness constant indicates that the binding forces between the ions are quite strong.

1. Introduction

Non Linear Optical materials play an important role in the field of telecommunication, optical switching and optical processing. In recent years several studies dealing with organic, inorganic and semiorganic molecules and materials called nonlinear optics (NLO) are being reported, due to the increasing need for cheap and easily processable materials for photonics applications. The nonlinear responses induced in various molecules in solution and solids are great interest in many field of research [1, 2]. Organic materials possess good optical tansmission characteristics, ultrafast non linear response time and high optical damage threshold; they attracted chemists and material scientists. But organic materials are soft in nature due to weak vander walls and hydrogen bonds with conjugated π electrons by which these materials are constituted.

Thiourea molecules are an interesting inorganic matrix modifier due to its large dipole moment and its ability to form and extensive network of hydrogen bands [3]. Thiourea crystals also exhibit pyroelectric effect, which is utilized in infrared (IR), ultraviolet (UV), scanning electron microscopy (SEM) detection and infrared imaging [4] Spectroscopic and microscopic studies of thiourea single crystals were performed by Patel et al [5]. In view of finding good quality thiourea crystal, in the present investigation, an attempt has been made to grow an optical quality thiourea single crystal by low temperature solutions growth technique. In addition, XRD, FT-IR, optical studies, and mechanical hardness, etc. have been performed in details.
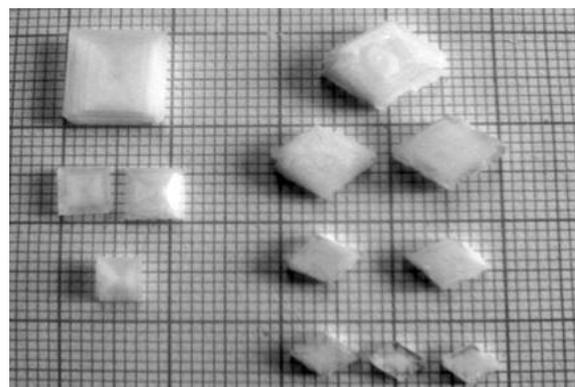
Fig. 1. Photograph of single crystal of Thiourea + Sulphuric acid.
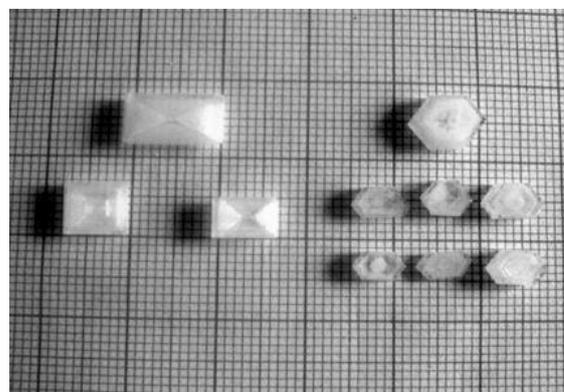
Fig. 2. Photograph of single crystal of Thiourea + nitric acid.

2. Experimental

2.1. Crystal growth

The growths of thiourea single crystals were carried out from concentrated sulphuric acid and nitric acid solution by Solvent evaporation technique. 100 ml saturated solutions were prepared at room temperature and then filtered to remove any insoluble impurities. The spontaneous nucleation was prevented during the filtration process. Seed crystals were prepared by isothermal condition. The saturated solutions were kept in the Petri dish and the outer face was covered by perforated transparent polythene paper or filter paper. The petri dishes were kept at the room temperature until small transparent well-shaped crystals obtained. Within first week, the seed crystals and single crystals were grown in the petri dishes. The growth period of single crystal takes within 2 weeks. The sulphuric acid and nitric acid doped thiourea crystals possess well defined morphologies with reasonable size of about $1 \times 1 \times 0.5$ cm^3, $1.1 \times 1 \times 0.4$ cm^3 and $1. 2 \times 0.7 \times 0.5$ cm^3, $1 \times 0.8 \times 0.6$ cm^3 along all the three crystallographic directions as shown in Fig. 1 and Fig. 2 respectively.

3. Results and discussion

3.1. X-ray diffraction

X-ray diffraction pattern for the single crystals of sulphuric and nitric acid doped thiourea crystals were carried out using Bruker-Nanius CAD-4 Diffractometer (MoKα-radiation). The lattice parameters were determined as: a = 5.493(1) Å, b = 7.655(3) Å and c = 8.561(3) Å, α = β = γ = 90° and cell volume equals to 360.0(9) Å^3 for the sulphuric acid doped thiourea crystal and a = 5.482(1) Å, b = 7.653(0) Å and c = 8.542(5) Å, α = β = γ = 90°, V = 358.4(2) Å^3 for the nitric acid doped thiourea crystal.The crystals exhibit orthorhombic crystal in nature.

3.2. FT-IR spectral studies

The Fourier Transform Infrared Spectroscopy is effectively used to identify the functional groups present in the crystals. The powdered specimen of thiourea from aqueous, sulphuric acid and nitric acid crystals has been subjected to FTIR analysis by PERKIN ELMER SPECTRUM RXI Fourier Transform Infrared Spectrophotometer using KBr pellet technique in the wavelength range between 400 and 4000 cm^{-1}. The observed bands along with their vibrational assignments have been tabulated as shown in Table.1. The comparative FTIR spectra of thiourea from aqueous, sulphuric acid and nitric acid are as shown in the Fig.3. Crystal structure investigations of thiourea have established the co-planarity structure of C, N and S atoms in the molecule [6]. In the complex, due to the double centers for thiourea, there is a possibility to coordinate with metal in two ways i.e.,

through nitrogen or sulfur [7] of thiourea. The high frequency N-H absorption bands in the region 3179 - 3395cm^{-1} in the spectrum of thiourea have not been shifted to lower frequencies on the formation of metal thiourea complex [8]. The FTIR spectra and assignment clearly indicate some of the functional groups of thiourea are altered by the addition of the dopants. Moreover the presence of absorption peak at 2360 and 2368 cm^{-1} confirms the presence of (C=NH$^+$), NH$^+$ stretching in the sulphuric acid and nitric acid doped thiourea crystal confirming that the dopants has entered into the thiourea lattice which is absent in the pure thiourea crystals respectively. NH$_2$ bending vibration at 1621 cm^{-1} of thiourea was shifted to 1616 and 1594 cm^{-1}. The N-H absorption bands in the high frequency region of thiourea were not shifted to lower frequencies.

Table.1. Assignments of IR band frequencies of Thiourea, Sulphuric and nitric acid doped thiourea crystal.

Thiourea cm^{-1}	Sulphuric acid doped thiourea cm^{-1}	Nitric acid doped thiourea cm^{-1}	Assignment
	3782		NH$_2$ asymmetric stretching
3395	3387	3391	NH$_2$ asymmetric stretching
3179	3175	3173	NH$_2$ stretching
2674	2678	2676	NH$_2$ stretching
	2360	2368	(C=NH$^+$), NH$^+$ stretching
2104	2107	2104	(NCN), NH$_3^+$ stretching
2033	2033		-
1621	1616	1594	NH$_2$ bending
1464	1464	1465	(NCN) asymmetric stretching
1395	1400	1388	(C=S) asymmetric stretching
	1199		NH$_2$ rocking
1089	1084	1089	(CN) stretching
729	728	728	(C=S) stretching
485	488	485	(NCS) asymmetric bending
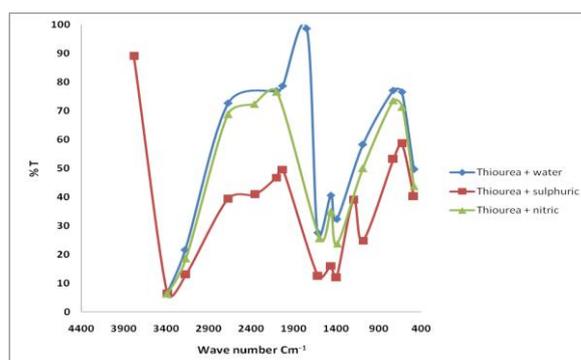
Fig. 3. FT-IR spectrum for Thiourea, Sulphuric and nitric acid doped thiourea crystal.

3.3. Optical studies

Optical transmittance spectrum analysis has been measured by using LAMBDA-35 UV-Vis spectrometer in the wave length range of 190 – 1100 nm. The UV-VIS spectrum gives limited information about the structure of the molecule because of the absorption of UV and visible light involves promotion of the electron in σ and π orbital from the ground state to higher energy states. The recorded absorption and transmittance spectrums of thiourea from aqueous, sulphuric acid and nitric acid are as shown in the Fig. 4. and Fig. 5 respectively and the lower cutoff wavelengths are around 250 nm, 250 nm and 252 nm respectively. The π electron dislocation is responsible for its nonlinear optical responses and absorption in near UV region [9]. The wide range of transparency of grown crystal is an added advantage in the field of optoelectronic application [10]. The grown crystals have got a low absorption and good transmission in UV –Vis and Near IR region.
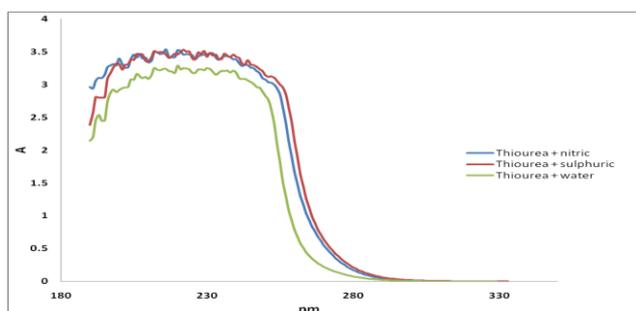
Fig. 4. UV-Vis absorption spectrum of Thiourea, Sulphuric and nitric acid doped thiourea crystal.
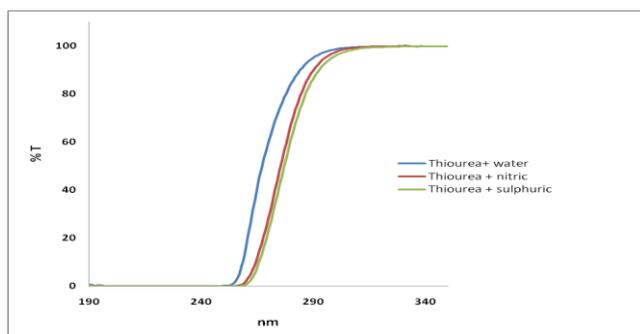
Fig. 5. UV-Vis transmittance spectrum of Thiourea, Sulphuric and nitric acid doped thiourea crystal.

3.4. Mechanical property

The micro hardness of a substance is an important parameter to define the strength of its material. This property is basically related to the crystal structure of the material or in other words, the way in which the atoms are packed and the electronic factors operating to make the structure stable [11, 12]. Elastic deformation developed in a material when subjected to indentation is directly proportional to the plastic deformation [13]. Hardness is a measure of the resistance to plastic deformation [14]. This permanent deformation can be achieved by indentation, bending, scratching or cutting. The hardness of the crystal carries information about the strength, molecular bindings, yield strength and elastic constants of the material.

Micro hardness studies were carried out in the grown crystals at room temperature using a micro hardness tester, fitted with a diamond pyramidal indenter attached to an incident light microscope. For static indentation test the load of different magnitudes have been applied in a fixed interval of time. Vickers microhardness values have been calculated by using the formula $Hv = 1.8544 \times P/d^2$ Kg/mm^2. Where Hv is the micro hardness number, P is the applied load in Kg, d is the mean diagonal length of the indentation impression in mm and 1.8544 is a constant of a geometrical fraction for the diamond pyramid. A graph has been plotted between hardness number (Hv) and applied load (P) as shown in Fig. 6. The non-liner behavior of the microhardness of the crystals may be due to cleavage plane of the sample. Hardness values of crystals differ from one plane to another which confirms the microhardness anisotrophy. This can be attributed to the work hardening of the surface layers. The relation connecting the applied load (P) and diagonal length (d) of the indenter is given by the Mayer Law [15]. $P = ad^n$.
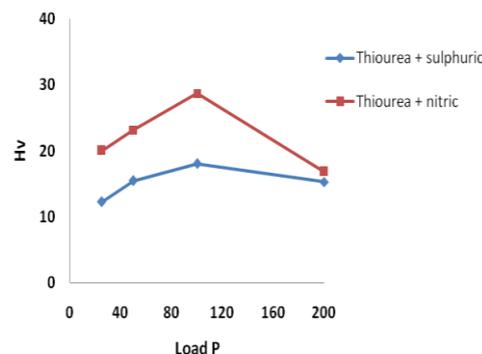
Fig. 6. Hv Vs Load P.

Where 'n' is the Mayer index or work hardening coefficient and 'a' is the constant for the given material. A graph has been plotted between log (P) Vs log (d) as shown in Fig.7.
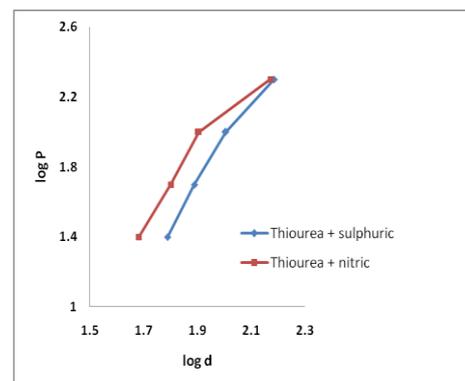
Fig. 7. log (P) Vs log (d).

The slope of the straight line by least square fit method gives Mayer index number / work hardening coefficient as 2.3283 and 1.8459 for sulphuric acid and nitric acid doped thiourea crystals respectively reveals that the materials are soft materials.

The microhardness value correlates with other mechanical properties such as elastic constants and yield strength (σ_y). Yield strength is one of the important property for device fabrication which can be calculated using the relation

$$\sigma_{y} = [Hv / 2.9]\{[(1-(2-n))][12.5(2-n) / (1-(2-n))]^{2-n}\}.$$

Where Hv is the hardness number and n is microhardening index. The yield strength σ_y were calculated for grown crystals and are given in the Table 2 and Table 3.

Table 2. Yield strength (σ_y) of the Sulphuric acid doped thiourea.

Sulphuric acid doped thiourea		
Load (P)	Hv	σ_y MPa
25	12.25	3.87
50	15.45	4.89
100	18.05	5.71
200	15.3	4.838

Table 3. Yield strength (σ_y) of the Nitric acid doped thiourea.

Nitric acid doped thiourea		
Load (P)	Hv	σ_y MPa
25	20	6.6225
50	21.50	7.1192
100	28.70	9.5033
200	16.80	5.5629

The elastic stiffness constant (C_{11}) were calculated for both the grown crystals using Wooster's empirical relation as $C_{11}= (Hv)^{7/4}$ [16 and 17]. The calculated stiffness constant for a load from 25gms to 200gms have been calculated and are given in Table 4 and Table 5. We have got a moderate value of C11, which indicates that the binding forces between the ions are quite strong.

Table 4. Stiffness constant of the Sulphuric acid doped thiourea.

Sulphuric acid doped thiourea		
Load (P)	Hv	C_{11} 10^{14}Pa
25	12.25	0.80211
50	15.45	1.2039
100	18.05	1.58
200	15.30	1.1836

Table 5. Stiffness constant of the Nitric acid doped Thiourea.

Nitric acid doped thiourea		
Load (P)	Hv	C_{11} 10^{14}Pa
25	20	1.89
50	21.50	2.1466
100	28.70	3.55
200	16.80	1.3940

4. Conclusion

Single crystals of sulphuric acid and nitric acid doped thiourea were grown by solvent evaporation method. The crystals exhibit orthorhombic structure. The various functional groups present in the crystals are analyzed by FTIR Spectrum. Their optical and mechanical properties are studied. The transparency nature of the crystal in the visible and infrared regions and it has a lower UV cutoff of around 252 nm are good expected characteristics for NLO materials. The microhardness study shows that hardness steadily increases, then decreases for higher loads. The work hardening index (n) showed that the crystals in present study are moderately softer substance. The value of stiffness constant indicates that the binding forces between the ions are quite strong.

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