INVESTIGATION ON GROWTH AND CHARACTERIZATION OF PURE AND TARTARIC ACID DOPED THIOUREA SINGLE CRYSTALS BY SLOW EVAPORATION TECHNIQUE

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Abstract

The growth of single crystals of pure and Tartaric Acid (TA)-doped Thiourea (TU) was accomplished by solvent evaporation. The grown crystals were characterised by Single crystal X-ray and X-ray powder diffraction. The crystallographic data shows the TA doped crystal structure and lattice parameters was changed from the pure TU grown crystal. The powder XRD study shows that the unit cell volume of the TA doped crystal was slightly decreased from the pure grown crystals. The FTIR spectrum shows the functional groups of the pure and TA doped TU grown crystals. The EDXA analysis find elements of the formation of TA in TU.

Key words:

Nonlinear optical material, conventional, Photon absorption, Tartaric acid, Thiourea

1. Introduction

Crystals are the unacknowledged pillars of modern technology. Without crystals, there would be no electronic industry, no photonic industry, no fiber optic communications, which depend on materials/crystals such as semiconductors, superconductors, polarizers, transducers, radiation detectors, ultrasonic amplifiers, ferrites, magnetic garnets, solid state lasers, non-linear optics, piezo-electric, electro-optic, acousto-optic, photosensitive, refractory of different grades, crystalline films for microelectronics and computer industries. Crystal growth is an interdisciplinary subject covering physics, chemistry, material science, chemical engineering, metallurgy, crystallography, mineralogy, etc. In the past few decades, there has been a growing interest on crystal growth processes, particularly in view of the increasing demand of materials for technological applications [1, 2]. Atomic arrays that are periodic in three dimensions, with repeated distances are called single crystals. It is clearly more difficult to prepare single crystal than poly-crystalline material and extra effort is justified because of the outstanding advantages of single crystals [3]. In recent years there has been considerable progress in the development of coherent UV sources based on non-linear optical processes. The demand for nonlinear optical crystals with superior properties is

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increasing due to quantum jump in the design of nonlinear optical devices with higher performance. With the progress in crystal growth technology, materials having attractive nonlinear properties are being discovered at a rapid pace [4-6]. To enable a material to be potentially useful for NLO applications, the material should be available in bulk single crystal form [7]. Thiourea is an interesting nonlinear optical (NLO) crystal and its metal complexes are the semiorganic NLO materials. Several researchers have grown and studied variety of thiourea complex NLO crystals and reported in the literature [8-11]. Also, the grown crystals of pure and TA doped TU were subjected to structural analysis, optical studies, mechanical studies, EDAX studies, thermal studies, Z-scan study and the obtained results are discussed in this chapter.

2. Experimental

2.1. Materials

All the reagents used in the present study were of analytical grade Thiourea and Tartaric acid (TA). The solvent used in all the experiments was double-distilled water.

2.2. Solubility studies

The solubility studies on pure and TA doped urea was separately conducted by conventional method for various ranges of temperatures such as 25°C,30°C,35°C,40°C,45°C and 50°C and shown in the fig.1. The solubility studies shows that all the materials possess positive temperature coeffiecient of solubility.It was also found that the addition of TA slightly increased the solubility of urea.
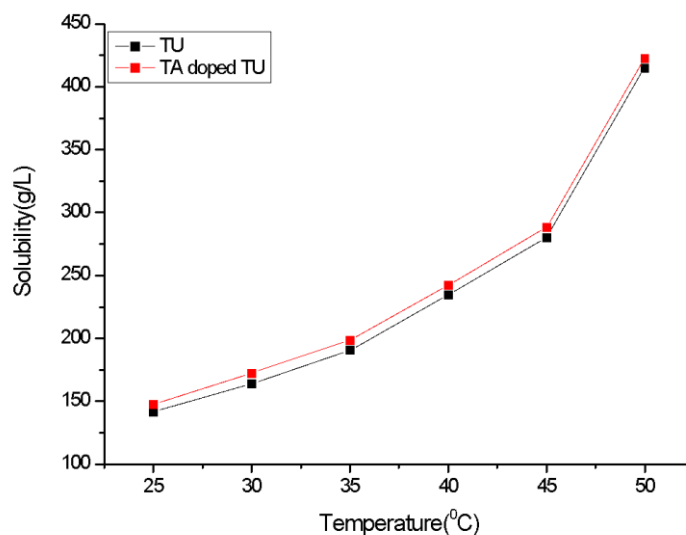

Fig. 1. Solubility curve of TU and TA doped TU

2.2. Crystallisation of pure TU and TA doped TU

300 ml of saturated solution of TU solution was prepared and distributed equally (150ml each) in two beakers of crystallizers. TU, was synthesized and used as the dopant 0.5 mole%

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of TA were added in one beaker containing the saturated solution. The solution was stirred well and adding drops of triple distilled water till the complete dissolution of dopant. The pH of the pure and TA doped TU solution was measured as 6.8 and 6.2.The crystallizers were covered with perforated polythene paper and kept in an constant temperature bath below Tc,29°C.Crystallization was initiated by isothermal slow evaporation of the solvent. Self-nucleated seed crystals were formed in all the crystallizers and it grows as the solvent evaporates. Pure and TA doped TU crystals were harvested after a period of 21 and 50 days and shown in figure 2 (a) and (b). The morphology of the TU crystals changed as the concentration of the dopant increased.
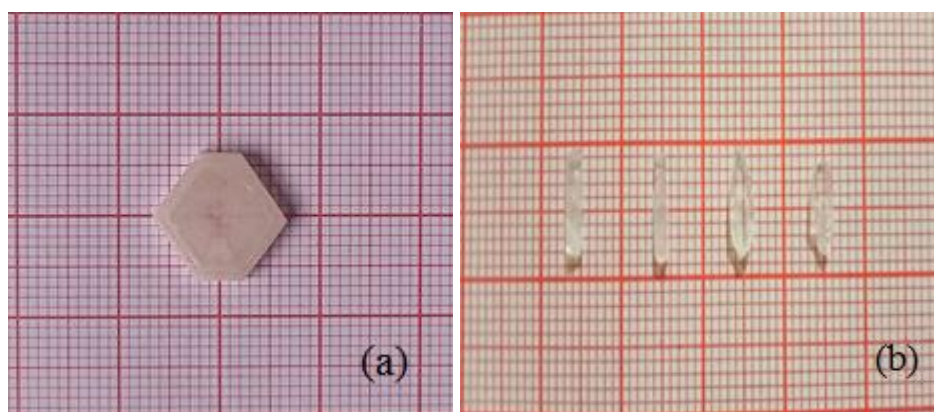

Fig. 2.Crystal habit of (a) TU; (b) TA doped TU

3. RESULTS AND DISCUSSION

3.1.1. Single Crystal X-Ray Diffraction Analysis

The grown pure and TA doped TU was confirmed by single crystal X-ray diffraction analysis. The single crystal data were obtained using a Bruker D8 QUEST single-crystal X-ray diffractometer. The result shows that the grown pure TU single crystal belongs to the orthorhombic system with the space group P. TA doped TU crystals are belongs to monoclinic crystal system with the space group P. the lattice parameters are found to be identical to the reported values (12). The obtained lattice parameters are shown in Table 1.

Table 1. Single crystal XRD lattice parameters of pure an TA doped TU

Parameter	Reported value	Present work of pure TU	TA doped TU
a (Å)	7.644	7.665	7.043
b (Å)	8.527	8.5539	8.336
c (Å)	5.493	5.4883	5.118
α (°)	90	90	90
β (°)	90	90	98.28
γ (°)	90	90	90
Volume (Å^3)	358	360	360
System	Orthorhombic	Orthorhombic	Monoclinic
Space group	P	P	$P2_1/a$

3.1.2. Powder X-ray Diffraction Analysis

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The structure of the grown pure and TA doped TU crystals was analyzed by powder XRD using PANalytical X'Pert Pro powder X-ray diffractometer with CuKa radiation. The powdered sample was analyzed between the diffraction angle ranges 10 to 90°. The recorded powder X-ray diffraction spectrum is shown in Fig.3.(a) and (b) Miller indices (h k l) are used to recognize the different planes of the samples. The observed diffraction peaks are related to the planes of the samples. The obtained (h k l) values are analyzed by using the unit cell software. The well-defined and sharp intensity peaks at definite 2θ angles show the good crystalline nature of the grown pure and TA doped TU single crystals.
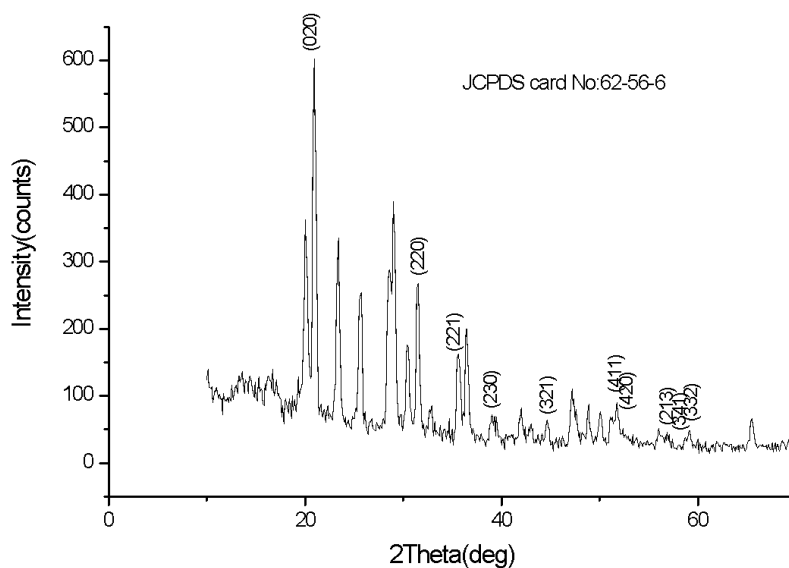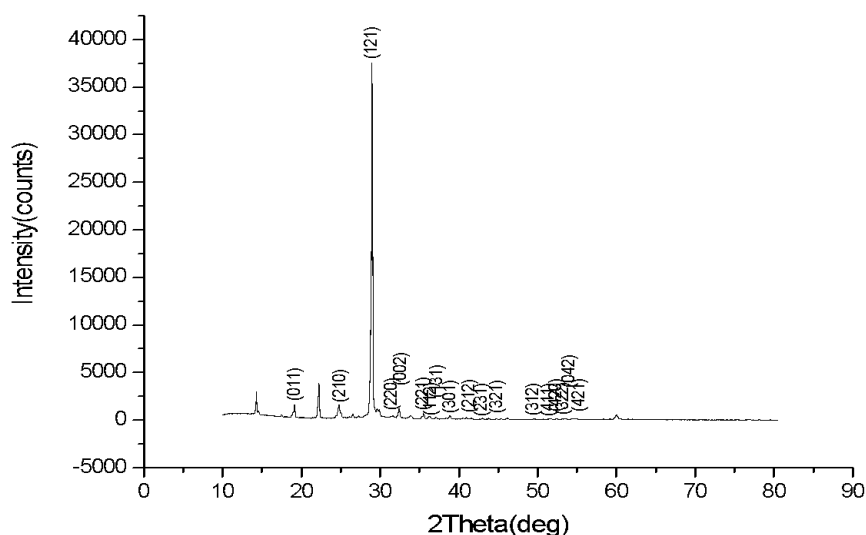

Fig. 3. (a) XRD spectrum of pure TU

Fig. 3. (b) XRD spectrum of TA doped TU

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Using Scherrer relation, the crystallite size was determined from the powder XRD data.

$$D = K\lambda/(\beta \, Cos\theta)$$

The full width half-maximum is represented as β and it is measured in radian, $\lambda = 1.5046$ Å, is the X-ray wavelength and θ is the Bragg's angle. The number of dislocation lines per unit area of the crystal, δ was calculated using the relation.

$$\delta = (1/D^2)$$

The dislocation density (δ) and the average crystallite size of the crystal were determined from the FWHM of the prominent peaks observed at in the powder XRD. The calculated very low value of dislocation density indicates the presence of negligible defects in the pure and TA doped TU crystal. The average crystalline size of pure urea is found to be as 30.78 nm. But the crystalline size of the TA doped urea is increased to 52.13 nm which confirms the presence of TA in the crystal lattice of TU (Table. 2). Also the dislocation density of TU is smaller than that of doped TA crystal.

Table 2: Calculated value of Average Crystalline size and Dislocation density results.

XRD parameters	Pure TU	TA doped TU
Average crystalline size in nm	30.78 nm	52.13 nm
Dislocation density in nm^2	1.06×10^{-3} m^2	3.68×10^{-4} m^2

3.2 Fourier Transform Infrared Analysis (FTIR)

The FTIR spectral analysis of the grown pure and TA doped TU crystals have been performed by KBr pellet technique in the wavelength range 500cm^{-1} to 4500 cm^{-1} using Perkin-Elmer FTIR spectrophotometer [Model 1605]. The various vibrational modes are presented in fig. 4. (a) and (b), respectively.
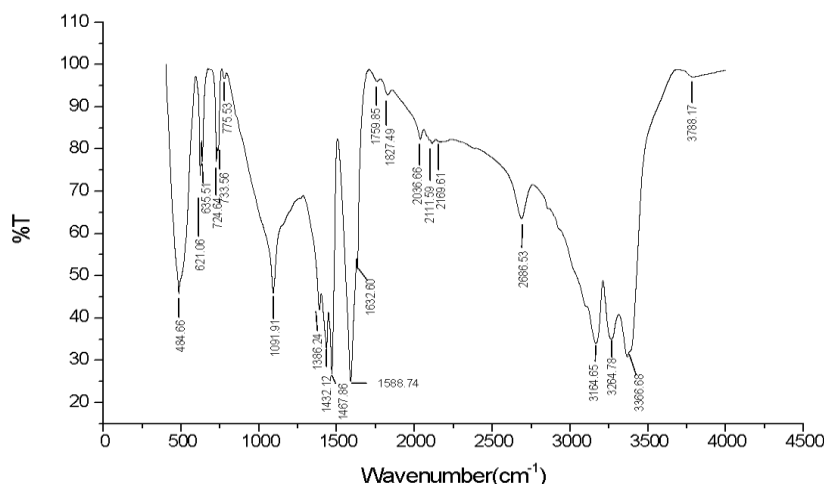

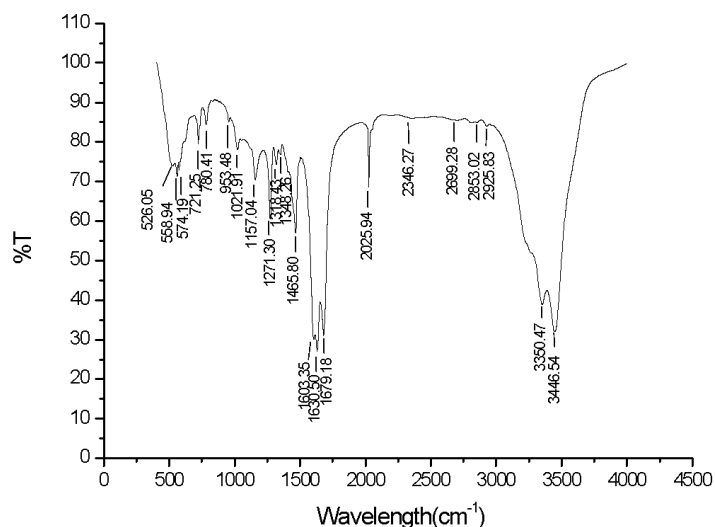Fig. 4. (a) FTIR spectrum of pure TU

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Fig.4. (b) FTIR spectrum of tartaric acid doped Thiourea

Table.3:FTIR spectral assignment for Pure and TA doped TU in cm^{-1}

Pure TU	TA doped TU	Spectral Assignment
484.66	-	N-C-N Bending
-	574.19, 558.94 and	C-I Stretch
621.06	-	S-O Stretching
635.51	-	C-C deformation
-	721.25	CH$_2$ Rocking vibration
724.67	-	In plane N-O bend
733.56 and 775.53	780.41	Aromatic out of plane C-H Stretching
-	953.48	C-C-C Stretch
-	1021.91	Si-O-Si Asymmetric Stretch
1091.91	-	C-O-C Asymmetric Stretching
-	1157.04	C-N-C Asymmetric Stretch
-	1271.30	C-N Stretching
-	1318.43	C-O Stretching
-	1348.26	NO$_2$ Symmetric Stretch
1386.24	-	C=S Asymmetric Stretching
1432.12	-	C-N Stretching
1467.86	1465.80	C=S Stretching
1588.74	-	N-S Scissoring
-	1603.35	Aromatic ring modes
	1630.50	C=C Stretching
1632.60	-	N-H Bending
1759.85 and 1827.49	1679.18	Symmetric C=O Stretching
-	2025.94	C≡N Stretch
2036.66	-	CH$_2$ rocking
2111.59 and 2169.61	-	C≡C Stretching

2300-3500	2300-3500	O-H, N-H and C-H Stretching
3788.17	-	O-H and C-H Stretching

The FTIR spectra of the grown pure and TA doped TU crystals are represented in fig. 4. (a) and (b). The spectra of the pure TU and TA doped TU are assigned to the N-C-N bending characteristic form present at peak 484.66 cm^{-1},C-I Stretching characteristic form present at peak 502.09 cm^{-1}, S-O stretching characteristic form present at peak 621.06 cm^{-1}, C-C deformation characteristic form present at peak 635.51 cm^{-1}, CH_2 Rocking vibration characteristic form is present at peak 721.25 cm^{-1} , In plane N-O bend characteristic form present at peak 724.67cm^{-1}, , Aromatic out of plane C-H stretching characteristic form is present at peaks of 733.56 cm^{-1} 775.53 cm^{-1} and 780.41 cm^{-1} , C-C-C Stretch characteristic form present at peak 953.36 cm^{-1}, Si-O-Si Asymmetric Stretch characteristic form present at peak 1021.91 cm^{-1}, C-O-C Asymmetric stretching characteristic form present at peak 1091.91 cm^{-1}, C-N-C Stretching Asymmetric stretching characteristic form present at peak 1157.04 cm^{-1}, C-N Stretching characteristic form present at peak 1271.30 cm^{-1}, C-O Stretching characteristic form present at peak 1318.43 cm^{-1} , NO_2 Symmetric Stretching characteristic form present at peak 1348.26 cm^{-1}, C=S Asymmetric Stretching characteristics are present at peak 1386.24 cm^{-1}.N-O Stretch characteristic form present at peak 1403.02 cm^{-1}, Acid in plane O-H Bend characteristic form present at peak 1417.90 cm^{-1}, C-N stretching characteristic form is present at peak 1432.12 cm^{-1}, C=S Stretching characteristic form is present at peak 1467.86 cm^{-1} 1467.86 cm^{-1},N-S scissoring characteristic form is present at peak 1588.74 cm^{-1},Aromatic ring modes characteristic form is present at peak 1603.35 cm^{-1}, C=C Stretching characteristic form is present at peak 1630.50 cm^{-1}, N-H Bending characteristic form is present at peak 1632.60 cm^{-1}, Symmetric C=O stretching characteristic form is present at peaks 1679.18 cm^{-1}, 1759.85 cm^{-1} and 1827.49 cm^{-1}, C≡N Stretch characteristic form present at peak 2025.94 cm^{-1},CH_2 rocking characteristic form is present at peaks 2036 cm^{-1}. C≡C stretching characteristic form is present at peaks 2111.59 and 2169.61 cm^{-1} NH and CH stretching characteristic forms are present at peak 2300–3500 cm^{-1} and O-H and C-H stretching characteristic forms are present at peak 3788.17 cm^{-1} [13-19], some peaks are absent from the TA doped TU and Pure TU grown crystals. The FTIR spectral assignments of pure and TA doped TU are shown in table 4. So the pure TU is incorporated with the TA doped TU to form a grown crystal.

3.3. Energy Dispersive X-ray Analysis

The chemical characterization of pure and TA doped TU was done by energy dispersive X-ray analysis and the spectrum is presented in fig.5.(a) and (b).
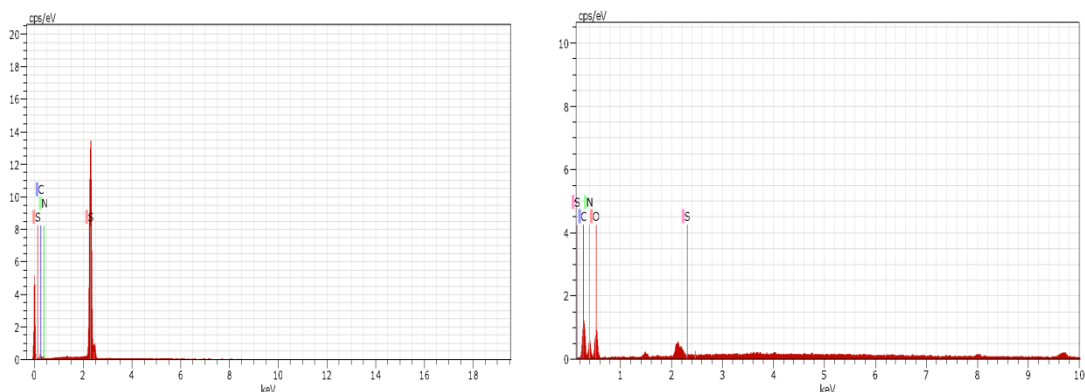
Fig. 5.(a) and (b) EDAX analysis of pure and TA doped TU crystal

It was investigated that 37.33 atomic weight % of TA is found in the TA doped TU. This study confirms that that TA was incorporated in TU. The relative concentration of the various elements found in pure and TA doped TU is expressed in terms of atomic weight % and weight %and is presented in table.4.

Table 4. EDAX data

Elements	Pure TU		TA doped TU	
	At.Wt. %	Weight %	At.Wt. %	Weight %
C	31.21	18.89	30.16	25.60
N	33.02	23.31	32.51	32.18
S	35.77	57.80	0.00	0.00
0	-	-	37.33	42.22

CONCLUSION

Pure and TA doped TU could be grown in various dimensions. The change in morphology of TA doped TU was noticed. The single crystal XRD study indicates that the grown crystals of pure and TA doped TU belong to orthorhombic and monoclinic c system with the space group P and the crystal system changed due to the dopant. The crystallographic data shows a slight variation from pure and TA doped TU in the lattice parameters and volume for the grown crystal. The powder XRD study shows that the unit cell volume of the TA doped crystal was slightly decreased from the pure grown crystals. Functional groups of the pure and TA doped TU were identified using FTIR spectral analysis. EDX analysis gives the information about the constituent elements in the TA doped TU and confirms the presence of oxygen in the crystal lattice.

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