STRUCTURAL, OPTICAL AND ELEMENTAL CHARACTERISTICS OF PURE AND TARTARIC ACID DOPED UREA SINGLE CRYSTALS

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Abstract

The growth of single crystals of pure and Tartaric Acid (TA)-doped urea was accomplished by solvent evaporation. The grown crystals were characterised by Single crystal X-ray and X-ray powder diffraction. The crystallographic data shows a slight variation from pure and TA doped urea 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 and increased from the pure grown crystals. The FTIR spectrum shows the functional groups of the TA doped grown crystals. The EDXA analysis find elements of the formation of TA in urea.

Key words: Optical material, Tartaric Acid, Gravimetric, Structural resemblance, Urea

1. Introduction

In the past few decades there has been a growing interest on crystal growth processes, particularly in view of increasing demand of materials for technological applications. Organic materials have been extensively investigated due to their nonlinear optical coefficients being larger than these of inorganic crystals. Many novel organic crystals have been found shown to have potential applications in nonlinear optics[1,2,3].

Urea $(NH_2)_2$ CO crystallizes in a tetragonal space structure, D^3_{24} (P $\overline{4}2_1$ m) two molecules per unit cell [4]. Due to its structure and short- and long-range dipolar intermolecular interactions significant research has previously been done on interactions. The high non-linear optical coefficient of urea crystals was discovered using powdered samples at 1.06μm [5].

Recent research demonstrates that urea makes an outstanding second harmonic nonlinear optical crystal. More effectively than the well-known KDP isomorphs during production and

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sum frequency mixing in the ultraviolet (to 235 μm) [6,7,8]. Nevertheless, urea crystals exhibit hygroscopic characteristics, making it challenging to obtain crystals at larger sizes for the manufacture of devices. First, an effort has been undertaken to crystallise urea under ambient circumstances, taking into account the significance of these crystals in numerous fields. In the present investigation, pure and various mole percentages of TA of doped urea have been grown by solvent evaporation technique.

2. Experimental

2.1. Materials

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

2.2. Temperature dependence on solubility

The maximum amount of solute that dissolves in a known quantity of solvent at a certain temperature is its solubility. Temperature will affect solubility. In the present investigation, the solubility of urea and TA-doped urea was estimated at various temperatures ranging from 25ºC to 50ºC in steps of 5ºC by the gravimetric method and shown in fig. 1.
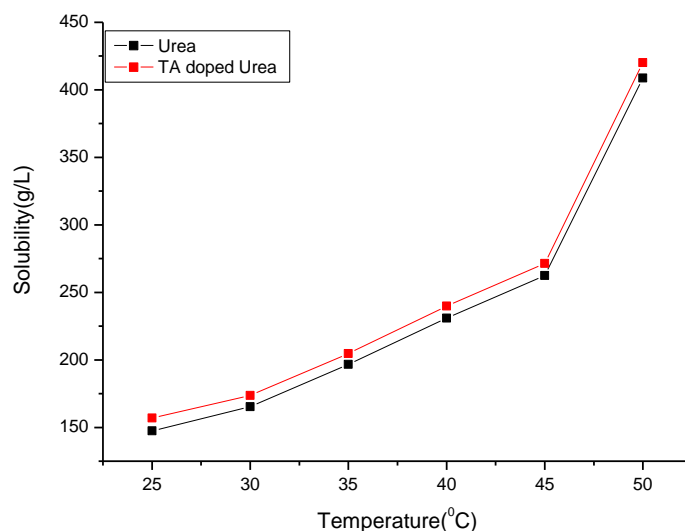

Fig. 1. Solubility curve of urea and TA doped urea

The collected data shows that the solubility of urea increases with an increase in temperature; the addition of TA to the pure urea solution increased the solubility and had a positive temperature coefficient of solubility.

2.3. Crystal growth

100 ml of saturated solution of urea was dissolved in double-distilled water using a magnetic stirrer at a constant rate for 6 hours at a temperature of 30º C. After attaining saturation, the solution was filtered using Whattman filter paper of porous size 11.5mm. A clean and dry 250-ml beaker was used in the present investigation. 50 ml of the saturated solution was

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taken from two such bakers. One beaker was left as standard for pure urea solution. In the other beaker, the solution was doped with TA. All the crystallizers were covered with perforated polythene paper and kept on a vibration-free platform. The self-nucleated urea crystals grew in the solution over the course of five days, fully matured pure urea and 50 days, fully matured TA doped urea could be grown. The self-nucleated urea crystals grew in the solution over the course of five days before being extracted and depicted in the Figure 2. (a) and (b). The morphology of the urea crystals changed as the concentration of the dopant increased.
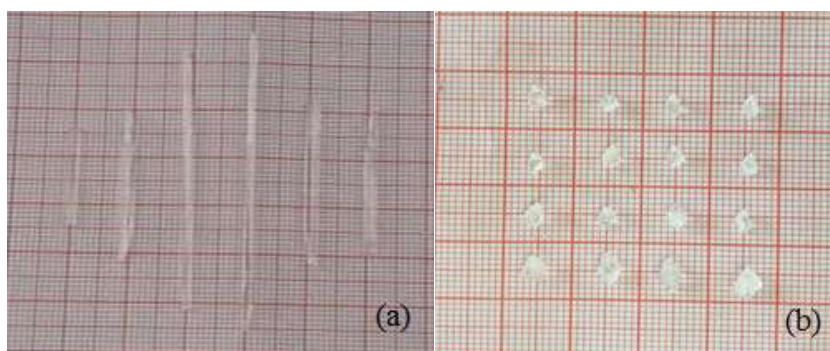

Figure 2. Crystal habit of (a) urea; (b) Tartaric acid doped urea

3. RESULTS AND DISCUSSION

3.1. Structural analysis

3.1.1. Single crystal XRD study

The grown crystals were subjected to single-crystal X-ray diffraction analysis using a Bruker D8 QUEST single-crystal X-ray diffractometer to determine the cell parameters and it reveals that the pure urea crystals are belongs to tetragonal crystal system , TA doped urea crystals are belongs to orthorhombic crystal system with the space group P. The lattice parameters of pure urea were found to be a = 5.712 Å, b = 5.712 Å, c = 4.670 Å, α = 89.78º, β = 89.78º, γ = 89.73º and the cell volume is V = 152.4 Å^3. The lattice parameters of TA doped urea were found to be a = 7.650 Å, b = 7.853 Å, c = 11.071 Å, α = 90º, β = 90º, γ = 90º and the cell volume is V = 665 Å^3. In case of the doped samples, a slight variation in the cell parameters is observed, which may due to the incorporation in urea. This analysis revealed that the pure urea, TA doped urea crystals change the crystal system through there is a small change in the lattice parameters.

3.1.2. Powder X-ray diffraction studies

The powder XRD diffraction is used to determine the crystallinity and phase purity.The grown pure and TA doped urea crystal was subjected to powder X-raydiffraction analysis by using PANalyticalX'Pert Pro powder X-ray diffractometer with CuKa radiation. The powdered sample was scanned in the range from 10° to 90°. The obtained powder X-ray pattern of pureand TA doped urea is shown in Fig. 3. (a) and (b). The obtained (hkl) values are in close agreement with the Joint Committee on Powder Diffraction Standards (JCPDS)

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file. The well-defined sharp Bragg's peaks at specific 2q angles show the good crystalline nature of the grown single crystal.
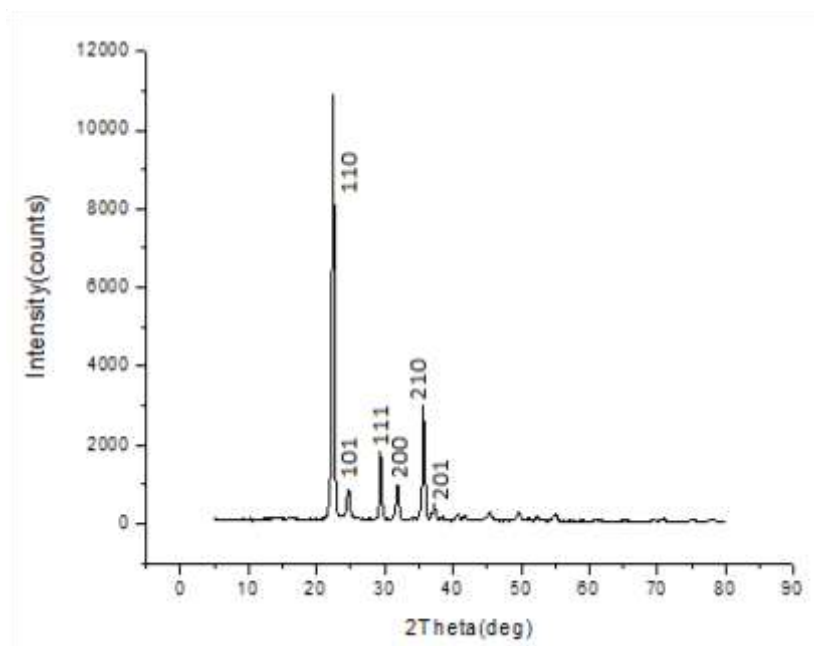

Fig. 3. (a) XRD spectrum of pure urea

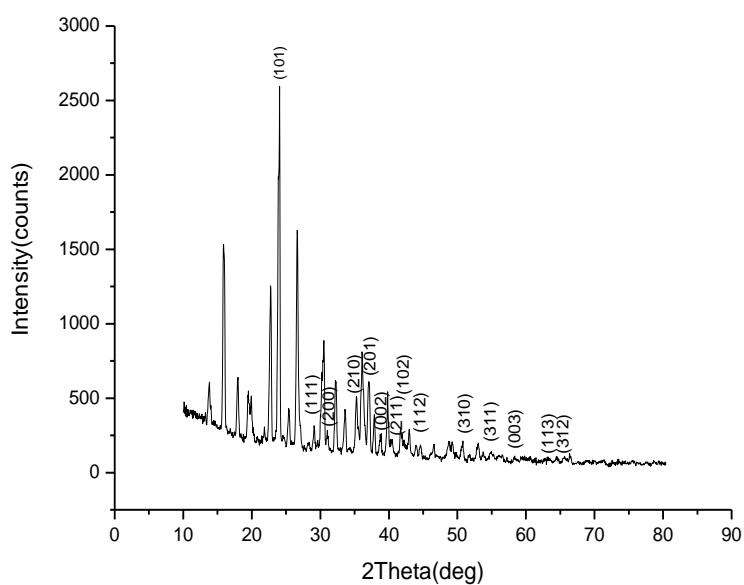Fig. 3. (b) XRD spectrum of TA doped urea

3.2. FTIR ANALYSIS

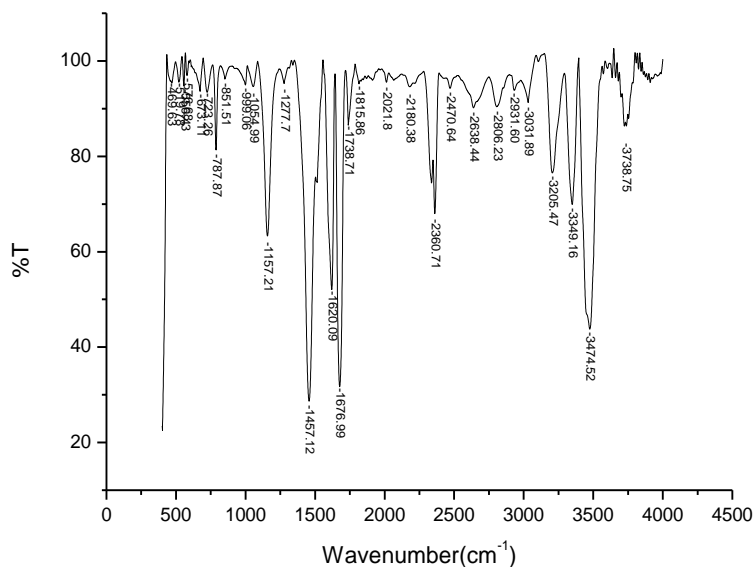The FTIR spectra of pure and TA doped urea are presented in fig. 4. (a) and (b), respectively.
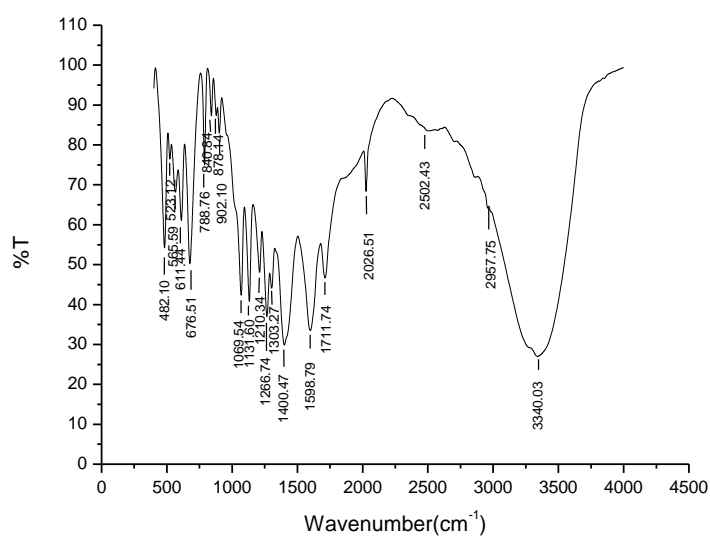

Fig. 4. (a) FTIR spectrum of pure urea

Fig.4. (b) FTIR spectrum of TA doped urea

Table 3. Wave number assignments for pure and TA doped urea in cm^{-1}

Pure urea	TA doped urea	Spectral Assignment
3738.75	-	O-H Stretching, C-H Stretching
3500-2300	3500-2300	NH&C-H Stretching Vibration
2180.38	-	C≡C Stretching
2021.80	2026.51	C≡N Stretching
1815.86 and 1738.71	1711.74	C=O Stretching
1676.99	-	C=C Stretching
1620.09	-	O-H bend(Ring modes)
-	1598.79	Aromatic ring modes
1457.12	-	NH$_3$ bending
-	1400.47 and 902.10	O-H In –plane bending vibration
-	1303.27	C-O Stretching
1277.75	1266.74	C-C-C Stretching
-	1210.34	CH$_3$-C-CH$_3$ Stretch
1157.21	-	C-N-C Asymmetric Stretch
-	1131.60	C-C-O Asymmetric Stretch
-	1069.54	C-N Stretching
1054.99	-	S=O Stretching
999.06	-	Out of plane C-H bending
	878.14	C-C-O Symmetric stretch
851.51	840.84	C-O-C Symmetric Stretching
787.87	788.76	Out of plane C-H bending
723.26	-	CH$_2$ Rocking vibration
673.11	676.51	O-H Out of plane bend
576.68, 556.43, 519.78	565.59 and 523.12	C-I Stretch
469.63	482.10	N-C-N Stretching

The FTIR spectra of the grown pure and TA doped urea crystals are represented in fig. 4. (a) and (b). The spectra of the pure urea and TA doped urea are assigned to the N-C-N Stretching characteristic form present at peak 469.63 cm^{-1},C-I Stretching characteristic form present at peak 576.68 cm^{-1}, O-H Out of plane bending characteristic form present at peak 673.11 cm^{-1}, C-H Wag characteristic form present at peak 635.51 cm^{-1}, CH$_2$ Rocking vibration characteristic form is present at peak 723.26 cm^{-1}, Out of plane C-H bending characteristic form is present at peaks of 787.87 cm^{-1} , C-O-C Symmetric Stretching characteristic form present at peak 851.51 cm^{-1}, C-C-O Symmetric stretch characteristic form present at peak 878.14 cm^{-1}, Out of plane C-H bending characteristic form present at peak 999.06 cm^{-1}, S=O Stretching characteristic form present at peak 1054.99 cm^{-1}, C-N Stretching characteristic form present at peak 1069.54 cm^{-1}, C-C-O Asymmetric Stretching characteristic form present at peak 1131.60 cm^{-1}, C-N-C Asymmetric Stretch characteristic form present at peak 1157.21 cm^{-1}, CH$_3$-C-CH$_3$ Stretching characteristic form present at peak 1210.34 cm^{-1} , C-C-C Stretching characteristic form present at peak 1277.75 cm^{-1}, C-O Stretching characteristics

are present at peak 1303.27 cm^{-1}. O-H In –plane bending vibration characteristic form present at peak 1400.47 cm^{-1} and 902.10 cm^{-1}, NH$_3$ bending characteristic form present at peak 1457.12 cm^{-1}[9], Aromatic ring modes characteristic form is present at peak 1598.79 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 1598.79 cm^{-1}, O-H bending (Ring modes) characteristic form is present at peak 1620.09 cm^{-1}, C=C Stretching characteristic form is present at peak 1676.99 cm^{-1}, C=O stretching characteristic form is present at peaks 1815.86 cm^{-1} and 1738.71 cm^{-1}[10], C≡N Stretch characteristic form present at peak 2021.80 cm^{-1}, C≡C Stretching characteristic form is present at peaks 2180.38 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 3738.75 cm^{-1} [11], some peaks are absent from the TA doped urea and Pure urea grown crystals. The FTIR spectral assignments of pure and TA doped urea are shown in table 2. So the pure urea is incorporated with the TA doped urea to form a grown crystal.

3.3. EDAX Analysis

The energy dispersive x-ray (EDAX) analysis is used to identify the elements of the grown pure and TA doped urea crystals find the elemental atomic weight percentage of the grown pure and TA doped urea crystals. The element analysis revealed that the elements are carbon, nitrogen and oxygen, which confirms that the samples are pure and TA doped urea. On comparing the elemental data of pure grown crystal, the elements of carbon have increased atomic weights and weight percentages in the TA doped urea. The elements of nitrogen have decreased atomic weights and weight percentages in the TA doped urea. The oxygen element atomic weight and weight percentages are increased and decreased in TA doped urea. This analysis revealed the elements in the grown pure and TA doped urea crystals and the atomic and weight percentages was slightly changed due to the incorporation of TA doped urea. Normally, this analysis does not acknowledge the hydrogen element. So that was the reason pure and TA doped urea element of hydrogen are not presented in the EDAX data of pure and TA doped urea and crystal in Table 3. and Fig. 5.(a) and (b) also
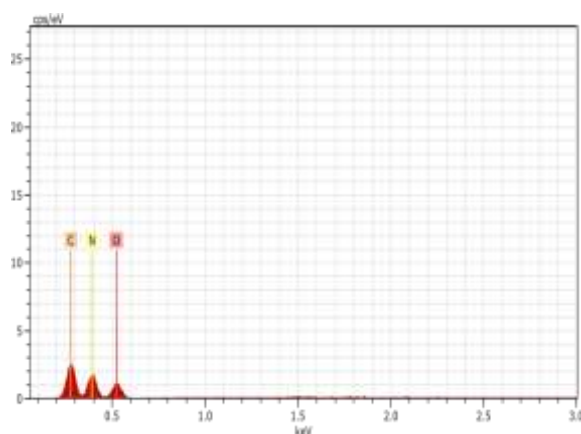

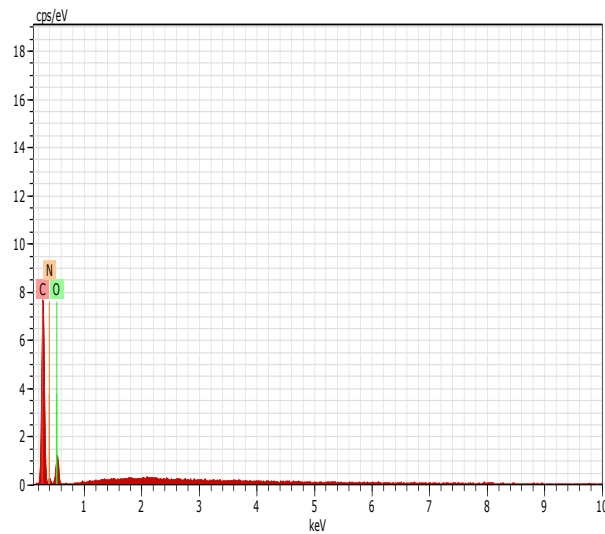Fig. 5.(a) EDAX spectrum of pure urea crystal

Fig 5.(b). EDAX spectrum of TA doped urea

Table 3. EDAX data of pure and TA doped urea grown crystals

Elements	Pure TU		TA doped urea	
	At.Wt. %	Weight %	At.Wt. %	Weight %
C	29.11	25.09	64.74	25.60
N	45.22	45.44	12.67	32.18
0	25.67	29.47	22.49	42.22

Table 3.shows that in pure and TA doped urea crystals, the present elements, such as carbon, nitrogen and oxygen were found. But in the pure and TA doped urea, the atomic and weight percentages are slightly changed, that was due to the incorporated in the parent element.

CONCLUSION

Pure and TA doped urea could be grown in various dimensions. The change in morphology of TA doped urea was noticed. The single crystal XRD study indicates that the grown crystals of pure and TA doped urea belong to tetragonal and orthorhombic 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 urea 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 and increased from the pure grown crystals. The FTIR spectrum shows the incorporation of the TA doped grown crystals. The EDXA analysis confirms the formation of TA in urea.

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