GROWTH AND CHARACTERIZATION OF UREA-THIOUREA DOPED TRIGLYCINE SULPHATE SINGLE CRYSTALS

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ABSTRACT

Ferroelectrics are an important class of electronic materials. Due to the demand of highly sophisticated radiation and thermal detectors,electro-optical devices,imaging,recording and other important applications in various sophisticated instrumentations, this field has gained significantly in its scientific and technological values. Glycine derivative ,triglycine sulphate (TGS) , a well known ferroelectric reflects a large pyroelectric coefficient and a high Volt/Watt sensitivity put in to thermoelectric detector. In the present study 0.5mole % urea(NH_2-CO-NH_2) and 0.5 mole% thiourea(NH_2-CS-NH_2) was put together and used as the double dopant.A single crystal with well defined crystal morphology was obtained.The grown crystal was characterized for their morphological,structural,optical, SEM,EDAX and non-linear optical properties.

Keywords

Amino acids,Urea,Thiourea, chiral carbon, non-centro symmetric, hydrophilic.

1.INTRODUCTION

In nature about 300 aminoacids occur. Most of the aminoacids are alpha aminoacids,which means that the amino group is attached to the same carbon atom which the carboxyl groups is attached. Generally aminoacids having an asymmetric carbon atom exhibit optical activity.Asymmetry arises when 4 different groups are attached to the same carbon atom. Aminoacids posses second harmonic generation because of the chiral carbon atom and crystallizes in non-centro symmetric space groups.

Among the twenty aminoacids , based on the structure, Glycine is the simplest aminoacid, hydrophilic in nature and has no asymmetric carbon atom and therefore shows no optical activity.To get non centro symmetric space groups selective acids such as sulphuric acid, phosphoric acids are used to convert glycine into non centro symmetric space group.

Triglycine sulfate (TGS) $(CH_2NH_2COOH)_3 \cdot H_2SO_4$, a ferroelectric discovered in 1956[1]. This noval material may be considered a unique material for pyroelectric uses [2,3]. TGS undergoes second order phase transition from paraelectric to ferroelectric state at Tc , 322 K which is followed by change of structural space group of symmetry from P21/m to P21.Lattice parameters of TGS at room temperature are a = 9.392 Å, b = 12.734 Å, c = 5.784 Å and monoclinic angle β = 109.45 º [4].

2.EXPERIMENTAL

2.1. Materials

Analar grade glycine, Concentrated sulphuric acid , and triple distilled water were used for the synthesis of TGS. Urea and Thiourea were used as the double dopants.

2.2. Material Synthesis

The compound,triglycine sulphate was synthesized using glycine and concentrated sulphuric acid in the ratio 3:1.The volume of concentrated sulpuric acid required was diluted with triple distilled water. As per the data given in the literature glycine was dissolved in diluted sulphuric acid [5]. The temperature of the solution was kept below 60°C. The following reaction is expected to take place giving the compound.

$3(NH_2CH_2COOH)+H_2SO_4 \longrightarrow (NH_2CH_2COOH)_3.H_2SO_4$

Prior to the crystal growth,the synthesized material was recrystallized several times to get the purified material.

2.3 Solubility Studies

The solubility of pure TGS was determined for various ranges of temperatures such as 30,35,40,45,50 and 55°C by thermograviometric method.The solubility of Urea-Thiourea doped TGS solution was also determined for the said ranges of temperature.It was found that both the pure and the doped TGS solution possess positive temperature coefficient of solubility.The solubility of the doped solution was found to be slightly increased in the presence of the two dopants.The temperature versus solubility of pure and doped TGS was presented in Figure 1

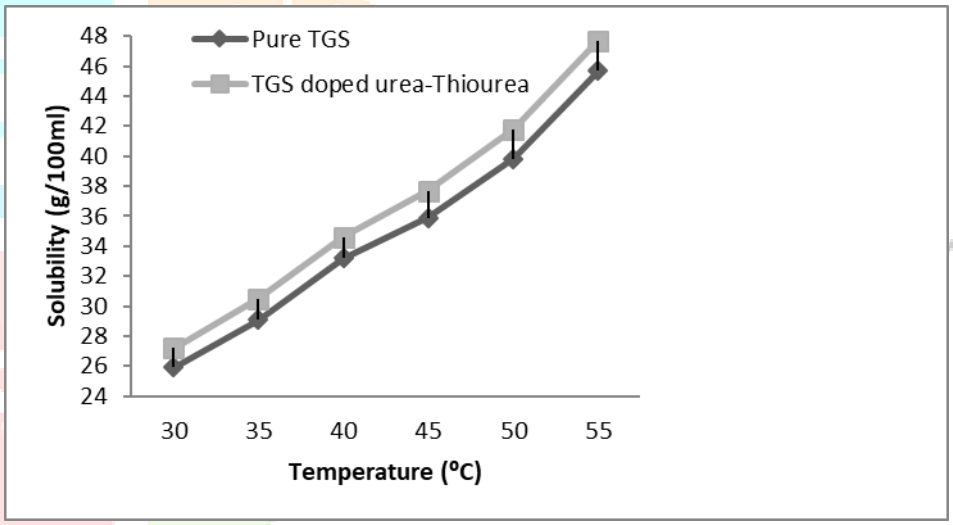


Fig.1. The solubility of pure and doped TGS

2.3. Preparation of urea -thiourea doped triglycine sulphate single crystals

In this experimentation, 200 ml of saturated solution of triglycine sulphate was prepared using the solubility data at 29°C. The solution was stirred well using a magnetic stirrer for 5 hours. 0.5 mole % of urea and 0.5 mole % of thiourea was simultaneously added as the additive in the prepared mother solution.The temperature of the solution was raised to 0.5° C and stirred well till the solute and the dopants dissolves. The solution was filtered using Whattmann filter paper. The filtered solution was transferred to a cleaned 250 ml beaker which acts as the crystalliser. The pH of the solutions was found to be 3.The beaker was covered with perforated polythene paper and it is kept in a vibration free platform.The solution was subjected to slow evaporation.As the solvent evaporates, a seed crystal is formed.After a period of 35 days a fully grown doubly doped triglycine sulphate single crystal could be grown.

3. RESULTS AND DISCUSSIONS

3.1. Morphological studies

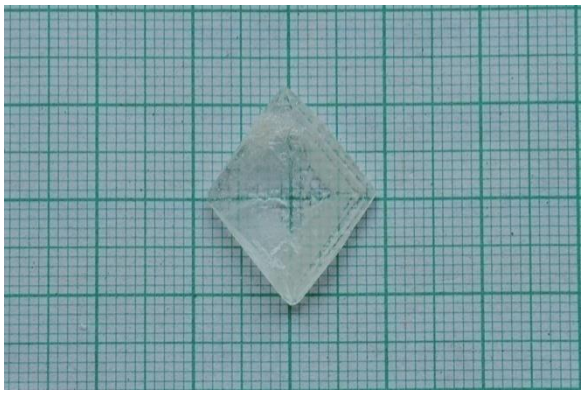
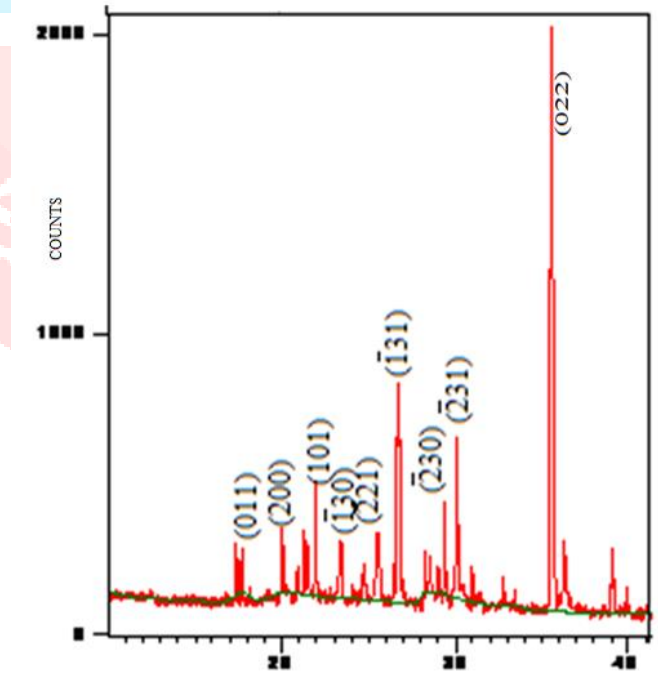


Fig.2. Morphology of Urea-Thiourea doped TGS

The morphology of the Urea-Thiourea doped TGS was found to be well faceted, transparent with sides of equal dimensions. While comparing with the morphology of pure TGS[6]some of the faces were disappeared and only the growth rate along four faces from the nucleation centre only exist. This may be due to the effect of impurities in the growth media has been noticed.

3.2. X-ray diffraction studies

X-ray diffraction pattern of the urea-thiourea doped triglycine sulphate crystal was recorded using XPERT-PRO-DIFFRACTOMETER system and shown in figure 3.



2θ(Degree)

Fig.3. XRD spectrum for the Urea-thiourea doped TGS

The various peaks obtained for the urea-thiourea doped triglycine sulphate single crystals were indexed. The JCPDS data for the pure triglycine sulphate and the computed crystallographic data for the grown urea-thiourea doped triglycine sulphate single crystals were presented in table1. The crystallographic data of the urea-thiourea doped triglycine sulphate was well agreed with the JCPDS data.

Table1.Unit cell parameters of urea-thiourea doped TGS

crystal	a(A°)	b(A°)	c(A°)	β (A°)	Calculated cell volume ($A^{\circ 3}$)
JCPDS data[7]	9.419	12.65	5.732	110.36	682.969
Urea+thiourea doped TGS	9.424	12.577	5.76	109.894	682.707

3.3. Fourier Transform InfraRed Analysis

The FTIR spectra for the urea-thiourea doped triglycine sulphate single crystals has been studied using BRUKER Optic GmbH spectrometer with model number-TENSOR 27 and presented in figure 4.

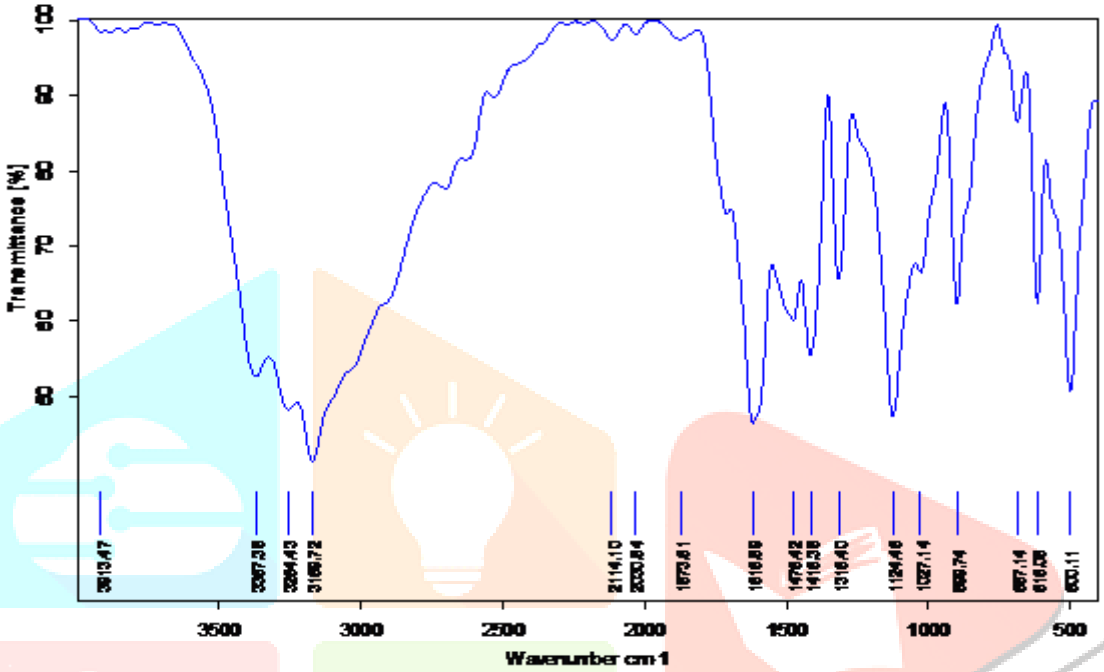


Fig 4. FTIR spectrum for the urea-thiourea doped TGS

The various functional groups pertaining to peaks in the FTIR spectra were assigned and presented in table2

Wave number (cm^{-1})	Assignment
3913.47	O-H stretching
3367.38	(NH_3^+) antisymmetric stretching
3254.43	(NH_3^+) symmetric stretching
3169.72	N=H stretching vibration
2114.10	O-H stretch of hydrogen bonded carboxyl group
2030.84	O-H stretch of hydrogen bonded carboxyl group
1873.61	C=O stretching
1616.89	C=Ostretching of COOH
1476.42	C=S stretching[8]
1415.38	C=O stretching
1315.40	C=O stretching
1124.45	S-Ostretching
1027.14	C=O stretching
899.74	NH_2 out of plane bending
687.14	S=O bending
616.08	S=O bending
500.11	NH_3 oscillation

3.4. Elemental Analysis

The energy dispersive analysis X-ray(EDAX) spectrum of urea-thiourea doped TGS has been recorded using Bruker Nano GmbH Berlin, Germany,Esprit 1.9 , and presented in Figure 5. EDAX result of the pure triglycine sulphate[6] and urea thiourea doped triglycine sulphate was presented in the table 3.

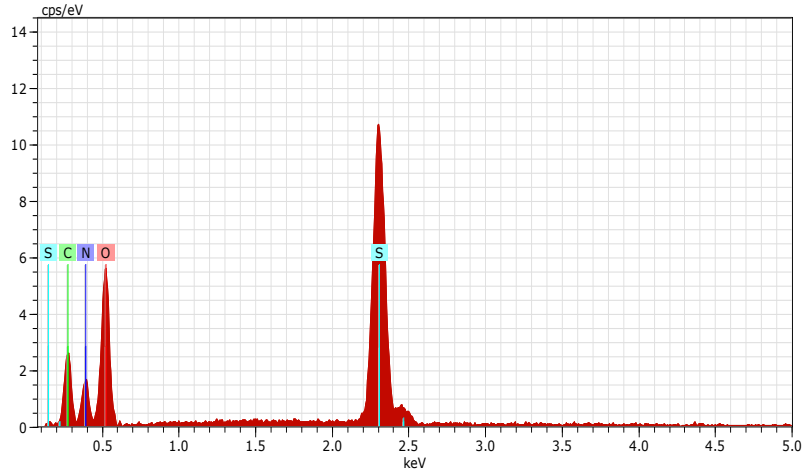


Fig. 5. EDAX spectrum of urea-Thiourea doped TGS

Table 3. EDAX data

Elements	*Pure Triglycine sulphate		Urea-Thiourea doped Triglycine sulphate		Differ in values	
	Atomic Weight %	Weight %	Atomic Weight %	Weight %	Atomic Weight %	Weight %
C	25.51	20.43	27.38	21.95	1.87	1.52
O	55.23	58.90	45.79	48.91	-9.44	-9.99
N	17.02	15.90	23.49	21.97	6.47	6.07
S	2.24	4.78	3.35	7.16	1.11	2.38

The various elements present in the urea-thiourea doped triglycine sulphate was compared with the pure TGS.The atomic weight percentage and the corresponding weight percentage of carbon,nitrogen and sulphur was found to be increased,may be the reason for the presence of urea and thiourea molecule.But there is a reduction in the atomic and weight percentage of oxygen atoms.This may be due to the replacement of oxygen atom by the nitrogen and sulphur atoms.

3.5. SURFACE ANALYSIS

The microtopographical feature of urea-thiourea doped triglycine sulphate single crystals was recorded by Scanning Electron Microscope and was displayed in figure 6.

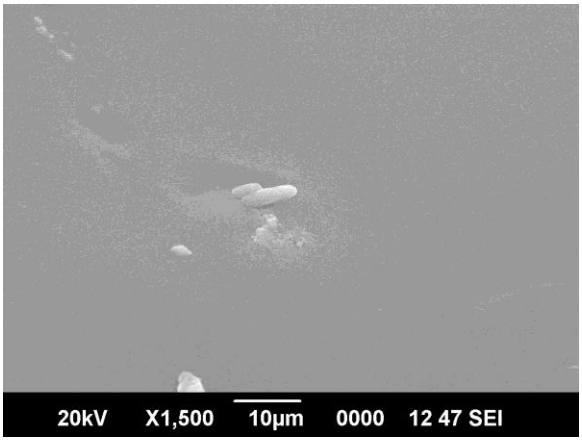


Fig .6. Microphotograph of urea –thiourea doped TGS

The surface was perfectly smooth as observed in the microphotograph.But a whitish region was observed on the smooth surface.This may be due to the effect of thiourea as the complexing agent.

3.6. Second Harmonic Generation Study

The nonlinear optical (NLO) property of the grown crystal was confirmed by Kurtz-Perry powder technique.Q-switched High energy Nd:YAG Laser(QUANTA RAY MODEL LAB-170-10) was used in the present study. An incident wavelength of light 1064 nm was allowed to fall on the samples. The emission of wavelength 532nm confirm both the urea-thiourea doped crystal posses NON LINEAR OPTICAL property.

4. CONCLUSION

In the present investigation the triglycine sulphate doped with urea-thiourea was successfully grown by solvent evaporation technique.The morphology of the doubly doped TGS was found to be well faceted, transparent with sides of equal dimensions. The crystallographic data of the doped TGS was well agreed with the JCPDS data. The various functional groups pertaining to peaks in the FTIR spectra were assigned and the presence of sulphur atoms in the doped crystal due to the dopant thiourea was confirmed.The increased in atomic weight percentage of carbon,nitrogen and sulphur and the decreased in atomic weight percentage of oxygen in the doubly doped TGS may be due to the effect of the urea-thiourea molecules.The microtopographical picture shows smooth surface of the doped crystal.The emission of wavelength 532nm confirms the NLO property of the doubly doped crystal.

5. REFERENCES

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