CRYSTALLIZATION AND CHARACTERIZATION OF LAURIC ACID DOPED TRIGLYCINE SULPHOPHOSPHATE SINGLE CRYSTALS

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ABSTRACT

In the past few decades advancement in crystal growth has lead to the discovery of new materials with enhanced non linear optical properties in the pure and doped form. In the present investigation an attempt has been made to substitute simultaniously phosphoric acid and sulphuric acid in glycine during synthesise of triglycine sulphophosphate and crystallised by solvent evaporation technique at constant temperature of 29°C.The effect of the different mole percentages of the dopant Lauric acid in the crystallisation of triglycine sulphophosphate was studied.Investigation shows that the crystal size was increased with the increase of the dopant concentration.The grown crystals were characterised for their structural,optical,elemental, and micromorphological features.

Index Terms

Physiochemical, phosphoric acid, Lauric acid, glycine triglycine sulphophosphate.

1.INTRODUCTION

Technology is based on single crystals of ferroelectric, semiconductor, superconductor, acousto optic, and non linear optical properties.Crystallization from aqueous solution by solvent evaporation is a simple technique.Crystals obtained by this technique possesses good qualities for various industrial applications. Triglycine sulphate (TGS) is a pyroelectric crystal used for infrared detectors and vidicons[1].Scientists discovered the depolarisation of TGS crystals and substituted phosphoric acid in glycine during synthesis[2,3].In the present investigation an attempt have been made to crystallize triglycine sulphophosphate(TGSP) in a recommended pH value 2.2[4] and various mole percentages of Lauric acid doped TGSP single crystals.

2.EXPERIMENTAL

2.1. Synthesis and crystallization

2.1.1. Triglycine sulphophosphate

Triglycine sulphate was synthesised using analar grade glycine and concentrated sulphuric acid in the ratio 3:1[5]. During synthesis the pH of the as prepared TGS solution was adjusted to 2.2 by adding a required quantity of phosphoric acid and glycine.

The following chemical reaction may be expected to yield triglycine sulpho phosphate.

$$3(NH_2CH_2COOH)+(H_2SO_4)_x+(H_3PO_4)_{1-x} \longrightarrow (NH_2CH_2COOH)_3.(H_2SO_4)_x(H_3PO_4)_{1-x}$$

Where x=0.5

The synthesised TGSP material was collected, dried and re crystallized in order to purify the material. TGSP was stored in a moist free atmosphere.

2.1.2 Solubility

Solubility study of TGSP was carried out using a hot-plate magnetic stirrer and a digital thermometer.50 ml double distilled water was taken in an air-tight container kept on the hot-plate maintained at 30°C.The synthesized salt of TGSP was added and stirred well till the solution reached saturation. The solubility of the saturated solution was determined by gravimetrically [6].The procedure to determine the solubility was repeated in steps of 5° C up to 55°C. The solubility of the Lauric acid doped TGSP can also be estimated for the same range of temperatures.Variation of solubility with temperature for TGSP and Lauric acid doped TGSP was studied and presented in figure 1. It was observed that both TGSP and Lauric acid doped TGSP possess positive temperature coefficient of solubility and the addition of Lauric acid slightly increased the solubility of TGSP.

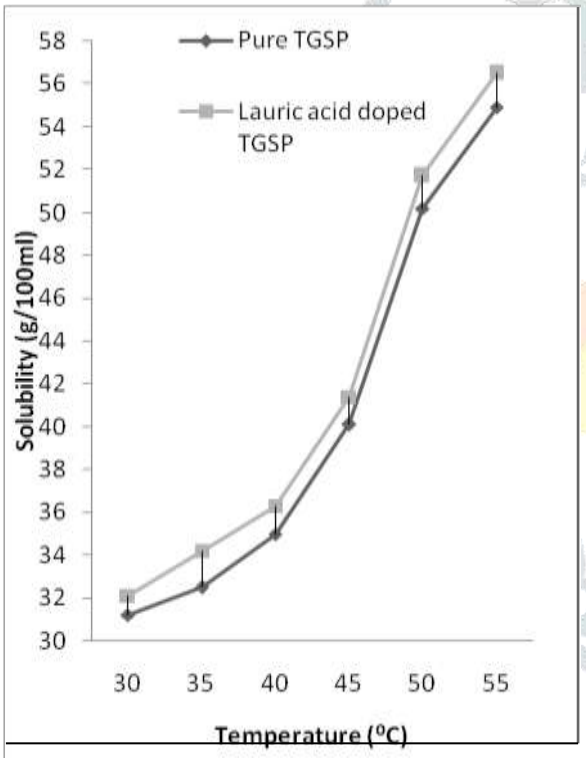

Fig. 1.Solubility of TGSP and Lauric acid doped TGSP

2.1.3 Crystallization

750 ml of Saturated solution of TGSP sample was prepared using the solubility data at 29°C.The saturated solution was stirred well using a magnetic stirrer at a constant rate for about 6 hours to get homogeneity. The solution was filtered using Whattman filter paper and the solution was equally distributed,150 ml each, in five 250ml beakers. 0ne beaker containing the TGSP solution was kept as standared.The pH of the TGSP was measured as 2.2. In the other beakers 0.25mole%, 0.5mole%,0.75mole% and 1mole% Lauric acid was added as the dopant, stirred well till the dopant dissolves and filtered.The pH of Lauric acid doped TGSP was found to be 2.1.

The crystalliser containing the solutions were covered with perforated polythene paper and kept in a water bath to maintain constant temperature of 29°C.The solvent evaporates slowly leads to super saturation followed by nucleation.The self nucleated small crystals grow in all the solutions.TGSP and Lauric acid doped TGSP crystals were harvested after a period of 40 days and depicted in figure 2a and 2b respectively.

3. RESULTS AND DISCUSSIONS

3.1. Morphological studies

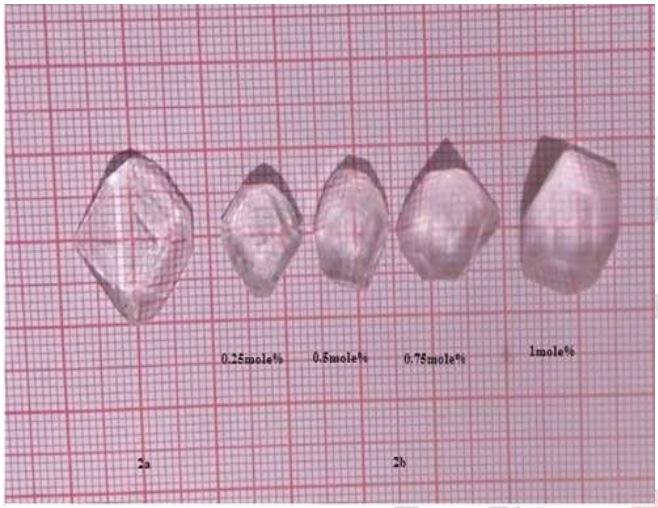

Fig.2a. TGSP and Fig.2b. Lauric acid doped TGSP

The physical appearance of TGSP was found to be transparent with dimension(2.0cm x1.6cm). Lauric acid doped crystals were found to be transparent with well defined faces.

Influence of concentration of impurities on morphology and size

The most important requirement of the crystals to be used for application is that they should be bigger in size and devoid of imperfection.The growth rate of any crystal is a function of a set of parameters like temperature,degree of supersaturation ,pH,concentration of impurities in the solution and other physio-chemical properties[7].The functional relation can be expressed as

R=F(t,S,pH,C)

Where R, the growth rate of the crystal and t,S,pH and C represents the temperature,super saturation the pH and concentration of the impurities in the solution respectively.In the present experimentation,all the growth parameters,t,S,pH were kept constant except the concentration of the dopant Lauric acid used.

An interface between a crystal and solution may be either atomically rough or in atomically smooth state.The smooth faces grow layer-by-layer. The new particles may be attached to the crystal at steps only.The crystals with smooth surfaces grow in the form of polygons[8].The polygon morphology with increase in size of the doped TGSP crystals may be due to the presence of Lauric acid in the crystallizing medium.

3.2. X-ray diffraction studies

Powder X-ray diffraction spectrum of the TGSP and Lauric acid doped TGSP crystal has been recorded using XPERT-PRO-DIFFRACTOMETER system with CuKα(Kα=1.50A°) radiation.The sample was scanned for a 2θ range 10-40° and at a scan rate 1°/min.The indexed diffractogram of TGSP and Lauric acid doped TGSP is shown in figure 3a and 3b.The crystal data is presented in table 1. The lattice parameters of

the grown TGSP was in good agreement with reported value .

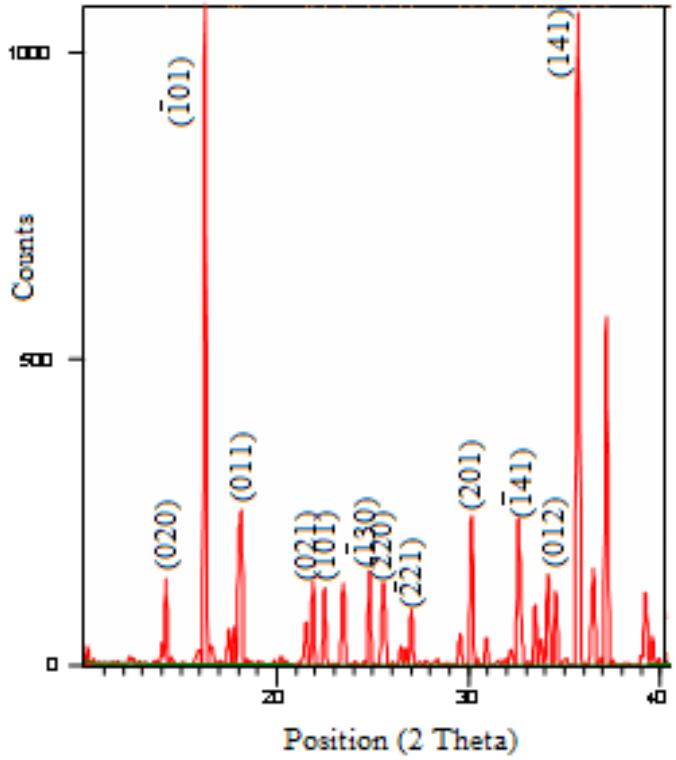

Fig. 3a.XRD pattern of TGSP

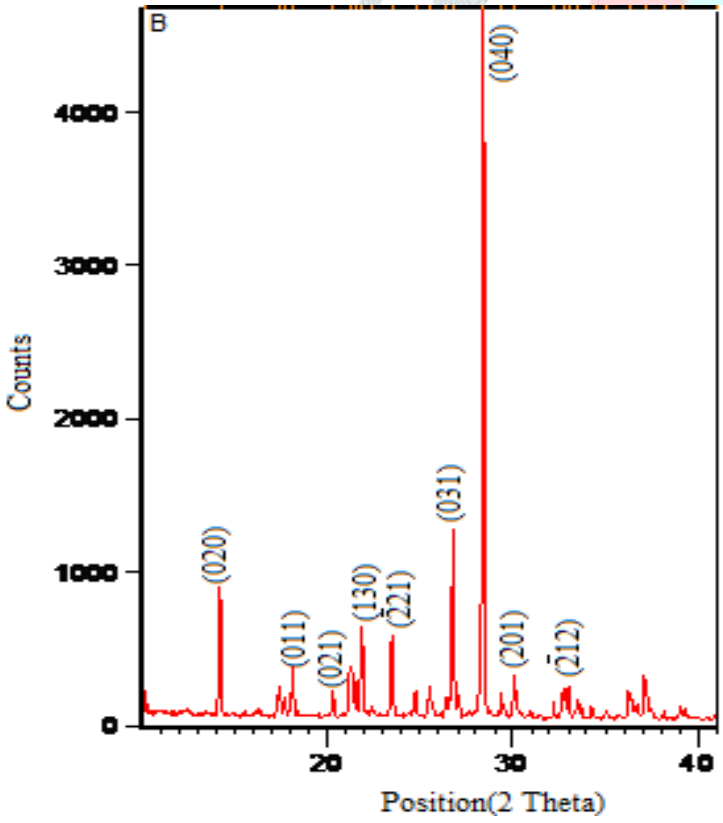

Fig.3b.XRD pattern of Lauric acid doped TGSP

Table 1.Cell parameters of TGSP and Lauric acid doped TGSP

Cell Parameters (A°)	TGSP (A°)[9]	TGSP (A°)	Lauric acid doped TGSP (A°)
a	9.43	9.38	9.33
b	12.65	12.64	12.60
c	5.73	5.71	5.78
α,β,γ(°)	90,110,90	90,110,90	90,110,90
CrystalSystem ,Space group	Monoclinic P21	Monoclinic P21	Monoclinic P21

3.3. Fourier Transform InfraRed Analysis(FTIR)

The FTIR spectral analysis of the grown TGSP and Lauric acid doped TGSP crystals have been performed by KBr pellet technique in the wavelength range 500cm^{-1} to 4000 cm^{-1} using BRUKER Optic GmbH spectrometer with model number-TENSOR 27. The various vibrational modes are presented in figure 4a and 4b and the assignments were presented in table2.

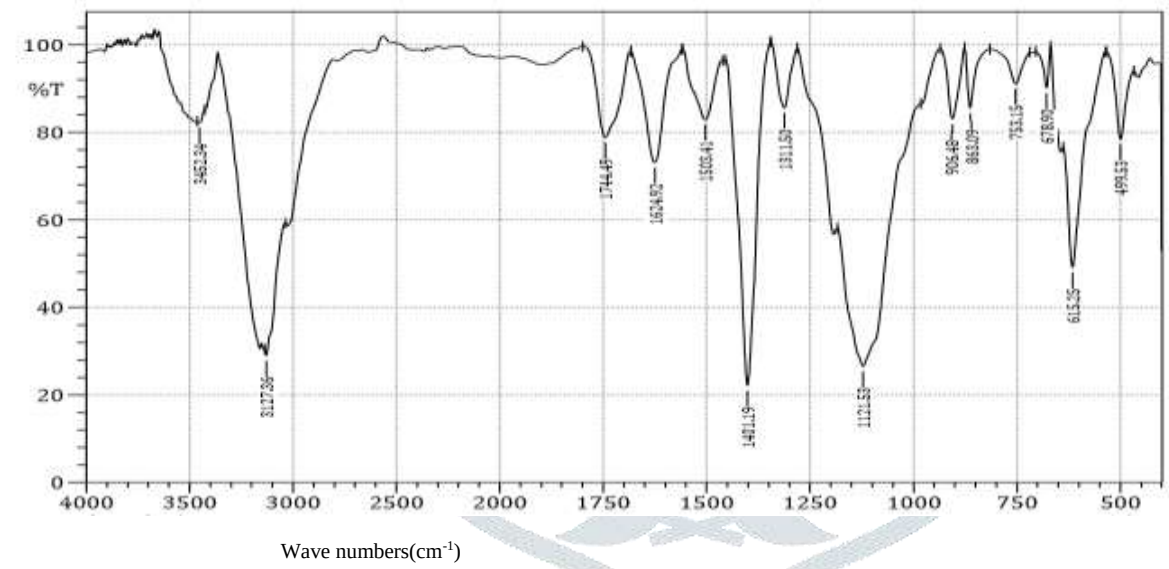

Fig. 4a. FTIR spectrum of TGSP crystal.

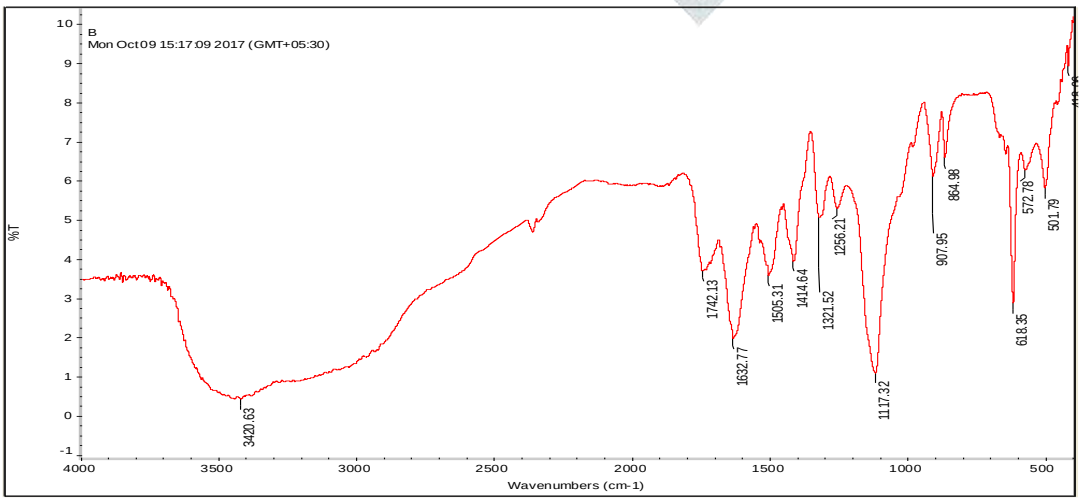

Fig. 4b. FTIR spectrum of Lauric acid doped TGSP.

Table2.Wave number assignments for TGSP and Lauric acid doped TGSP

Peak position in cm^{-1} TGSP	Peak position in cm^{-1} lauric acid doped TGSP	Assignment
3452.34,3127.36	3420.63	OH or NH and C-H
1744.49	1742.13	C=O stretch
1624.92	1632.77	NH_2 bending
1503.41	1505.31	NH_3bending
1401.19	1414.64	NH_4 bending
1311.50	1321.52	CH_2 bending of glycine and C-C stretch
1121.53	1256.21,1117.32	SO_4part of the molecule and CH_2 racking
906.48	907.96	C-C stretch
863.69	884.98	SO_4 stretch
753.15	-	NH_2 out of plane bend
678.90	618.36	S-O bend
615.25	572.78	C-N bending,NH_3^+oscillation
499.53	501.79	PO_4^{-3} bend

3.4. Elemental Analysis

The chemical characterization of this grown sample was done by energy dispersive x-ray analysis (EDXA).The obtained spectrum of TGSP and lauric acid doped TGSP was presented in Fig.5a and 5b.The various elements present in the grown crystals were identified and presented in table 3.

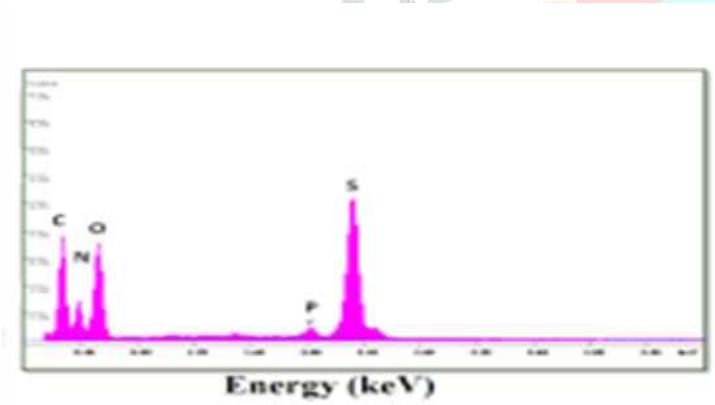

Fig.5a.EDXA spectrum of TGSP

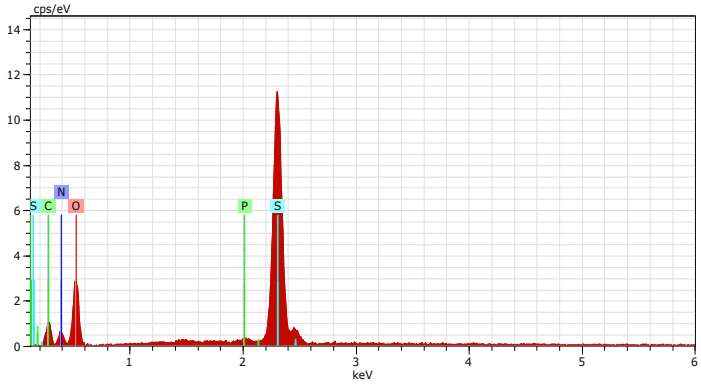

Fig.5b.EDXA Spectrum of lauric acid doped TGSP

Table 3. EDXA data

Elements	Pure TGS[10]		Pure TGSP		Lauric acid doped TGSP	
	Atomic Weight %	Weight %	Atomic Weight %	Weight %	Atomic Weight %	Weight %
C	25.51	20.43	39.33	32.47	28.24	21.81
O	55.23	58.90	43.12	41.93	45.13	46.42
N	17.02	15.90	15.66	15.24	19.91	17.93
S	2.24	4.78	1.75	3.89	6.63	13.66
P	-	-	0.14	0.47	0.09	0.18

On comparing the elemental datas of TGS and TGSP, 0.14 atomic weight percentage and 0.47 weight percentage of phosphorus was found in TGSP.This phosphorus element present in TGSP crystal shows that phosphate was substituted in TGS.The atomic weight percentage of carbon in lauric acid doped TGSP and the corresponding weight percentage was found to be reduced.Similarly the atomic and weight percentage of the phosphorus atoms present in Lauric acid doped TGSP was also found to be reduced .The atomic weight percentage and weight percentage of the elements such as oxygen,nitrogen and sulphur present in Lauric acid doped TGSP was found to be increased.This may be attributed to the incorporation of Lauric acid in the TGSP.

3.5. Surface Analysis

The scanning electron micro morphological patterns of TGSP and Lauric acid doped crystals were rec(rded using scanning electron microscopy and presented in figure 6a and 6b.

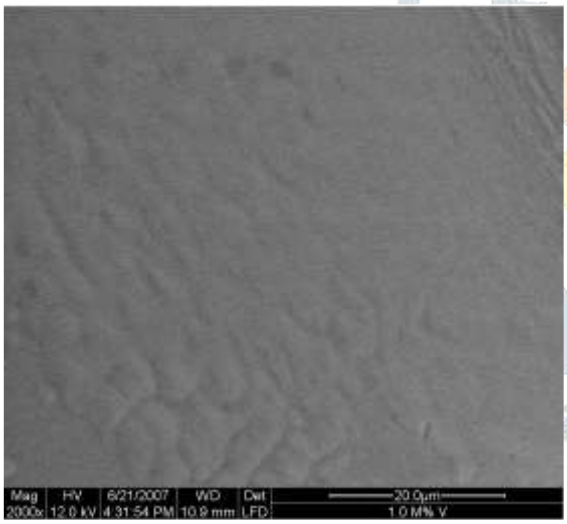

Fig.6a.SEM analysis of TGSP

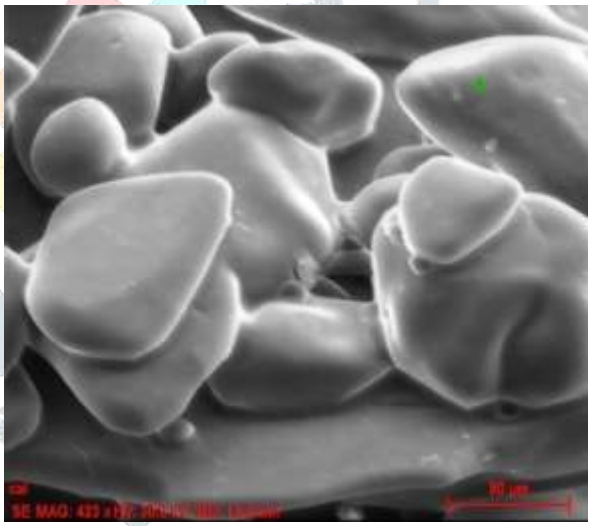

Fig.6b.SEM analysis of Lauric acid doped TGSP

On visualizing the micromorphological features of the TGSP, the surface was found to be smooth and devoid of any defects .This shows the purity of the grown TGSP single crystals.In the Lauric acid doped TGSP the surface was not smooth.But the presence of clusters of micro crystallites having both regular and irregular patterens were visualised.This may be due to the effect of dopant lauric acid.

4. CONCLUSION

Single crystals of TGSP and Lauric acid doped TGSP have been grown by slow evaporation technique.Investigation shows that TGSP and Lauric acid doped TGSP crystals were highly transparent with well defined facets. The polygon morphology with increase in size of the doped TGSP crystals may be due to the presence of Lauric acid in the crystallizing medium. X-ray diffraction studies confirmed that Lauric acid doped TGSP crystallized in monoclinic system with space group P21.FTIR spectral analysis confirmed the presence of functional groups in the crystals.EDXA shows the various constituent atom present in TGSP

and doped TGSP. SEM picture shows a smooth surface features of TGSP without any void.Doped TGSP shows the presence of some micro crystallites of the dopant lauric acid used.

5. REFERENCES

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