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Crystallization and Characterization of Zinc Thiourea Sulphate Doped Triglycine Sulphophosphate Single Crystals

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ABSTRACT

The rapid development of optical communication system has led to a demand for non-linear optical materials. Phosphorus substituted Triglycinesulphate is a ferroelectric material suitable for infra ray detectors. In the present study an attempt has been made to crystallize
Triglycinesulphophosphate single crystals doped Zinc thiourea sulphate. The effect of the dopant on the crystal habit and Non-Linear Optical property has been investigated. Habit modification was observed in the doped crystal. The NLO property of the doped TGSP was enhanced 2 times greater than the standard Potassium dihydrogen Ortho phosphate.

Keywords : Optical Communication, Triglycinesulphophosphate, Semiorganic, Zinc Thiourea Sulphate, Potassium Dihydrogen Ortho Phosphate

Introduction

Triglycinesulphate (TGS) is a derivative of a simplest amino acid glycine possess an important ferro-electric property discovered by Mathias,Miller and R.Emeika[1].TGS crystal shows a second order ferro-electric phase transition at the Curie point(Tc=49°C).Above the Curie point,it belongs to centrosymmetric point group P21/m of the monoclinic system and hence it lost the spontaneous polarization. Spontaneous polarization arises below Tc with lattice parameter values a=9.15A°,b=12.69A°,c=5.71A° and β=110°[2].Modification of ferroelectric properties doping with inorganic[3,4],amino acids[5,6],heavy rare earth ions [7,8],light rare earth ions [9] were reported by the scientists.Deuterated TGS crystals have also been grown and studied[10].

Phosphate was partially substituted for sulphate in the TGS crystal lattice (TGSP) by the investigators to solve the problem of microbial contamination of the solution with aging.It exhibits low dielectric permittivity and high pyroelectric coefficient[11]. Curie temperature of TGSP was found to be 51°C [12]. The growth kinetics and the domain structures of TGSP single crystals with various phosphate content was studied by Nakatani and Yoshio[13].It was found that there is no considerable structural change in Triglycinesulphophosphate substitution[14].TGSP crystals doped with amino acids such as L-alanine and L-asparagine have been investigated for the betterment in the pyroelectric property[15,16,17]. In the present study with an aim of enhancing the NLO properties of triglycinesulphophosphate single crystal,a semiorganic metal complex of thiourea, $Zn[CS(NH2)2]^3SO4$ is used as the dopant. The influence of the dopant on the crystal habit and NLO behavior of TGSP is discussed and reported in this paper.

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Experimental

Triglycinesulphophosphate was synthesized and 400 ml saturated solution was prepared as directed by the previous investigators using the recrystallized salt in triple distilled water at 30°C by constant stirring for 6 hours.The solution was preheated to a temperature 2.5°C higher than the saturated temperature to attain homogeneity and to avoid any spurious nucleation during filteration.The saturated solution was carefully filtered using Whattman filter paper and distributed equally (100ml each) in four identical crystallizers. ZTS, was synthesized by chemical reaction method and used as the dopant.1mole%,2mole% and 3mole% of zinc ZTS were added in three beakers containing the saturated solution and one beaker is left as standard.

The pH of the solution was measured as 2.2.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. TGSP and doped crystals were harvested after a period of 45 days and shown in figure 1a, 1b,1c and1d.

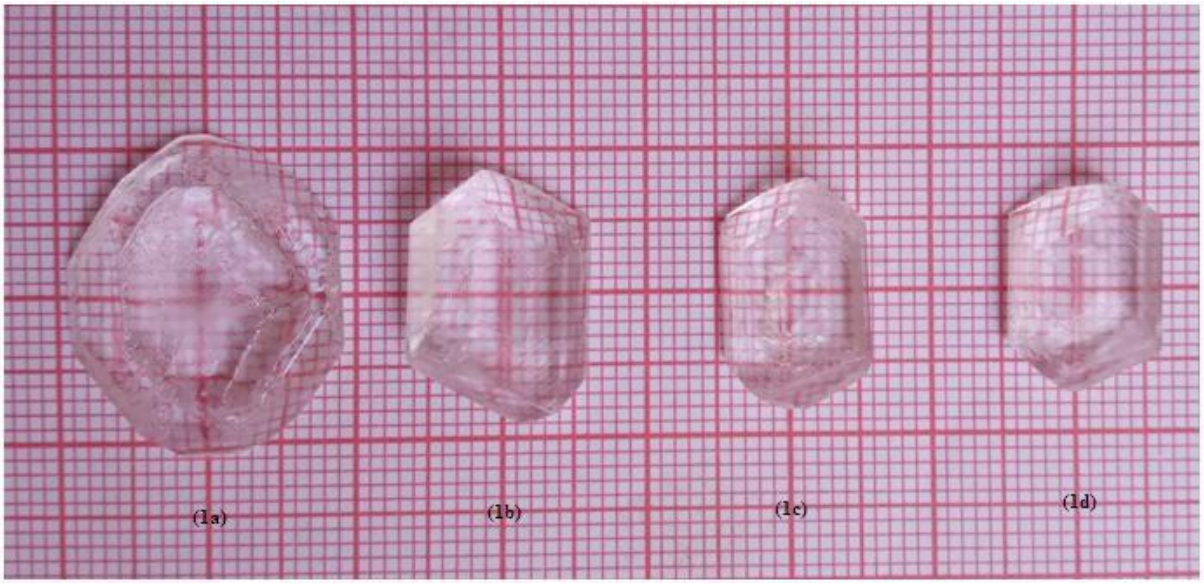

Fig1. Photograph showing the growth morphology of 1a. TGSP and 1b. 1mole%, 1c.2mole % and 1d.3mole % ZTS doped TGSP

The effect of dopant on the crystal habit

In single crystals, the crystal habit, the growth rate and other properties are influenced by a number of factors such as super saturation, temperature, pH, viscosity, initial status of the solution and the presence of impurities in the mother phase.All the factors are of considerable importance not only because of their influence on the physical and chemical properties of the resulting crystal but also a dominant role in controlling crystal growth behavior. The impurities can modify crystal morphology and growth rates as well as the stability of the solution during growth of the crystal.The effectiveness of different impurities changing the surface morphology different[18].Figure 1 shows TGSP crystals posses a well defined morphology as

investigated by the scientists[19]. The crystal habit of TGSP is like the crystal habit of TGS single crystals[20].But the Zinc thioureasulphate doped TGSP, the habit of the crystal was completely modified.

The habit modification can be explained as follows. The habit of a growing crystal is determined by the relative rates of growth of its faces.The slower the growth rate in the direction perpendicular to certain face,the larger that face appears.In the mother solution ZTS is in the ionic form as Zn^{2+} ion and thiourea and SO4. Zn^{2+} is a best growth inhibitor.It selectively adsorbs on certain crystal faces but not on other faces.The slower growing faces appear larger while the faster growing faces grows out of existence[21].The affected faces will appear larger than in non-affected faces.Thus the crystal habit will change as seen in the growncrystals.

Powder X-ray Diffraction Analysis

`The powder X-Ray diffraction pattern for the ZTS doped TGSP was recorded and presented in figure 2.The various diffraction peaks were indexed. The unit cell parameters were calculated as a=9.4029A°,b=12.569A°,c=5.769A° and β=110.061°. The unit cell parameters were compared with TGSP published Elsewhere[22].The unit cell volume was increased when compared with both TGS and TGSP as 13.988$A°^3$ and 4.819 $A°^3$ respectively.

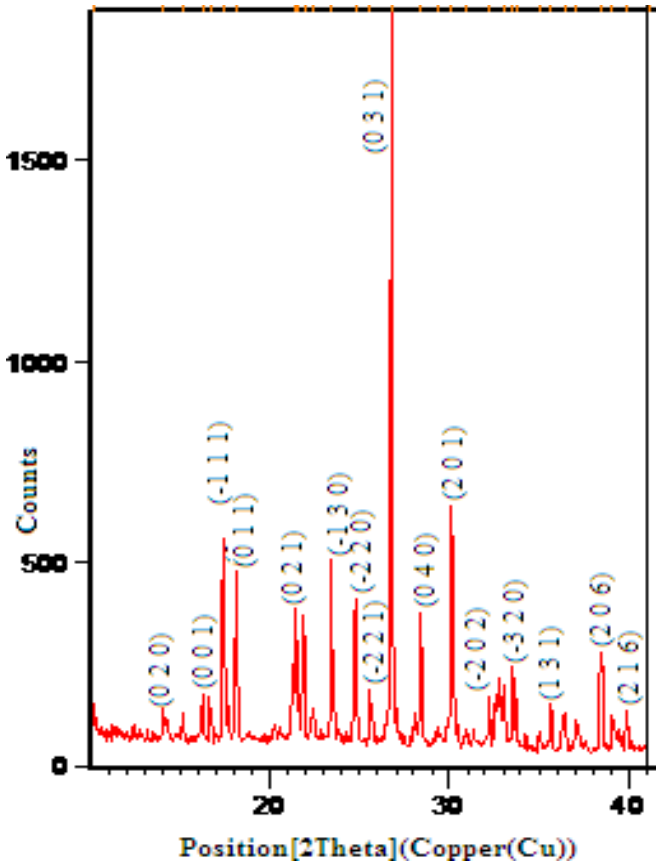

Fig.2 . XRD spectrum of ZTS doped TGSP

Fourier Transform Infrared Spectroscopic Studies

FTIR spectrum in an important tool to study the structure of a compound.In the present study FTIR spectrum was recorded in the range of 500-4000cm^{-1} and is presented in figure3.The various functional groups pertained to various wave numbers of TGSP doped with ZTS is assigned and is presented in table 1.

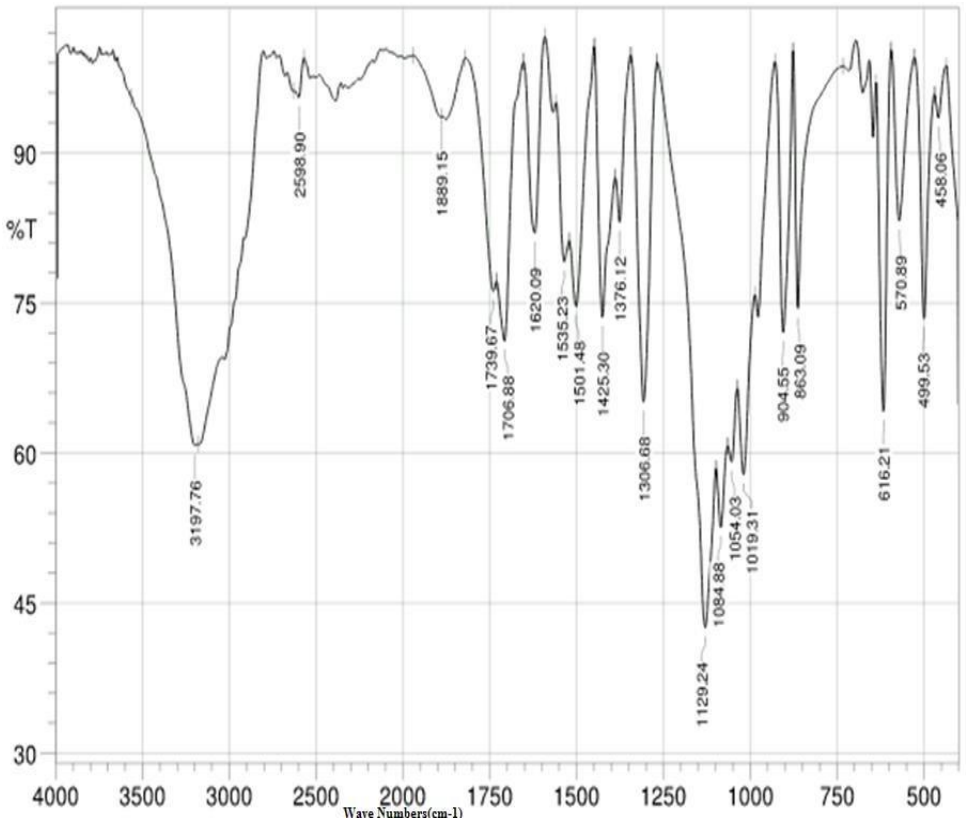

Fig.3.FTIR spectrum of ZTS doped TGSP

Table 1. Wave number assignments for ZTS doped TGSP

Peak position in (cm^{-1}) ZTS doped TGSP	Assignment
3197.76	OH or NH and C-H
2598.90	S-H Stretch
1889.15	Saturated symmetric C=O stretch
1739.67	C=O stretch
1706.88	C=O stretch
1620.09	NH_2 bending
1535.23	NO_2 Asymmetric stretch
1501.48	NH_3bending

1425.30	NH4 bending
1376.12	CH2 bending of glycine and C-C stretch
1306.68	C-O Stretch
1129.24	SO4 and CH2 rocking
1084.88,1054.03,1019.31	PO_4^{-3} Stretch
904.55	C-C stretch
863.09	SO4 stretch
616.21	S-O bend
570.89	C-N bending,NH_3^+oscillation
499.53,458.06	PO_4^{-3} bend

Energy Dispersive X-ray Analysis

The chemical characterization of doped TGSP was done by energy dispersive X-ray analysis and the spectrum is presented in fig4. The relative concentration of the various elements found in TGSP and ZTS doped TGSP is expressed in terms of atomic weight % and weight % and is presented in table 2.

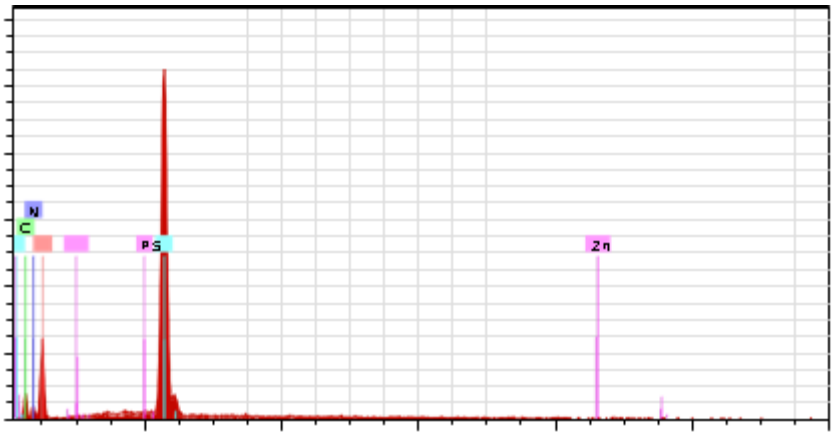

Fig. 4. EDXA spectrum of zinc thioureasulphate doped TGS

Investigation shows that 0.12 atomic weight % of zinc is found in the Zinc thiourea sulphate doped TGSP,confirms the incorporation of zinc in TGSP

Table 2. EDXA data

Elements	**Pure TGSP[22]**		**Zinc Thiourea sulphate doped TGSP**	
	Atomic Weight %	**Weight %**	**Atomic Weight %**	**Weight %**

C	27.31	20.25	30.30	23.13
O	46.82	45.86	44.26	45.01
N	16.13	13.95	17.45	15.53
S	9.32	18.46	7.92	16.14
P	0.44	0.83	0.04	0.07
Zn	-	-	0.12	0.03

Powder Kurtz method

An investigation on the Second Harmonic Generation of ZTS doped TGSP was measured by powder Kurtz method[23].The ratio of the fundamental and harmonic intensities generated was computed by the following equation gives the conversion efficiency of the sample.

$$\eta = I^2\omega \text{ Sample} / I^2\omega \text{KDP}$$

The computed SHG efficiency was compared with the well known inorganic NLO material KDP and investigated that the ZTS doped TGSP crystal has 2 times higher NLO efficiency than KDP.

SURFACE ANALYSIS

The microstructure of the grown Zinc thiourea sulphate doped TGSP was analysed using scanning electron microscope.The Scanning Electron Microscope (SEM) of Zinc thiourea sulphate doped TGSP single crystals were presented in fig.5.

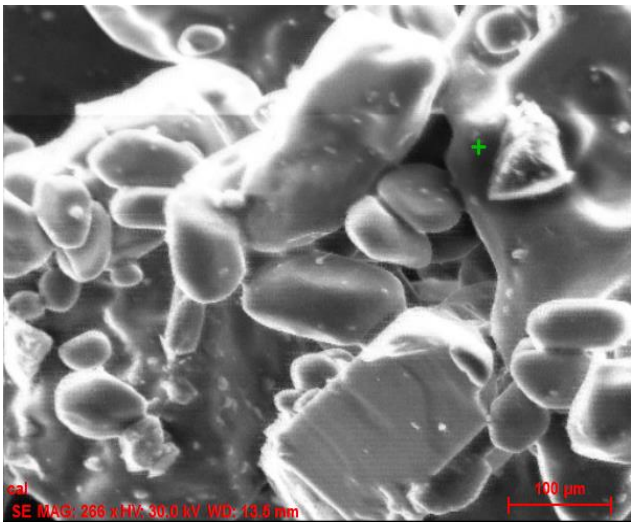

Fig. 5 : SEM analysis of ZTS doped TGSP

SEM microphotograph shows that clusters of regular and irregular shaped micro crystals are present over a smooth surface.

OPTICAL ABSORPTION STUDIES

Optical properties of crystalline materials gives information regarding the composition,nature and quality of the crystal.The U-V absorbtion spectra give information about the electrical nature of the material.An optically polished crystal single crystal was used for this study. In the present study UV spectra was recorded for Zinc thiourea sulphate doped TGSP and presented in fig.6.

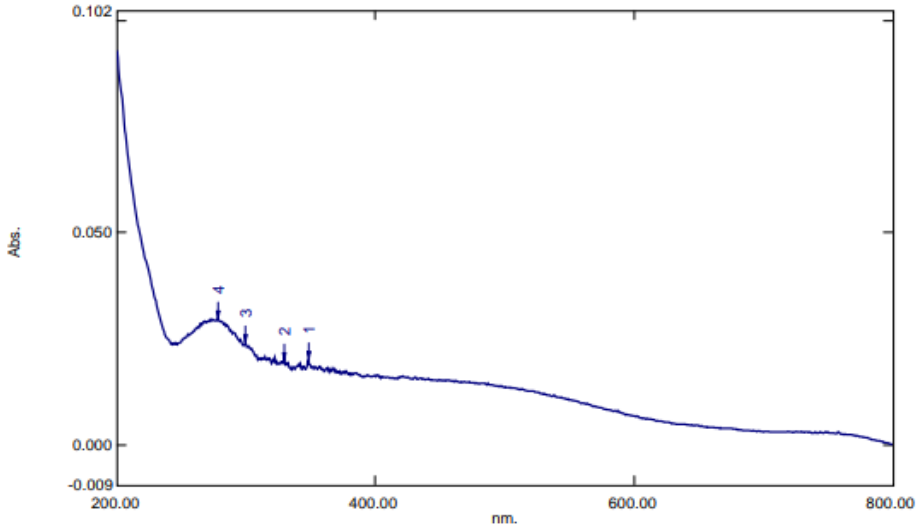

Fig. 6 : UV-Vis-NIR Absorption spectra of Zinc Thiourea sulphate doped TGSP

Plot of hυ versus $(\alpha h\upsilon)^2$ of Zinc Thiourea sulphate doped TGSP are shown in fig.7.

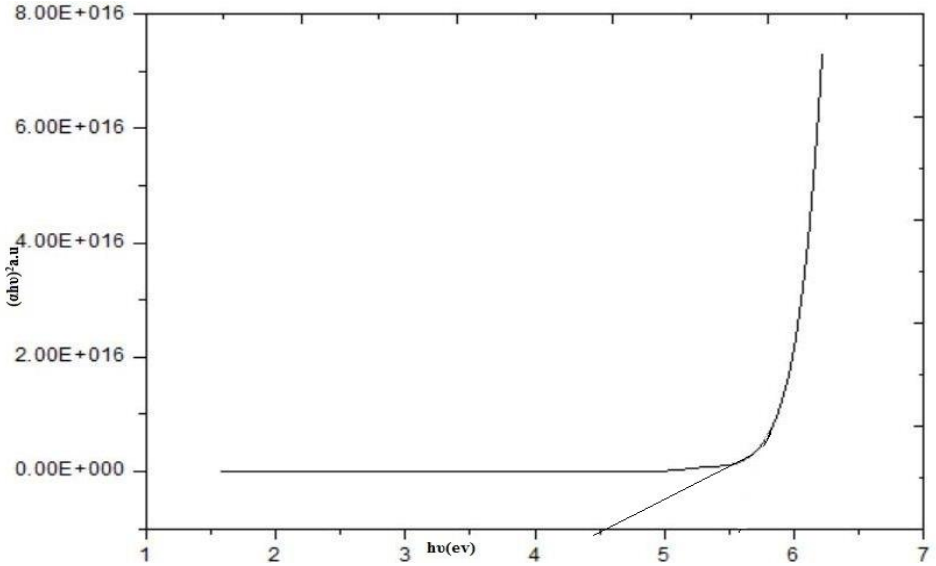

Fig. 7 : Plot of hυ versus $(\alpha h\upsilon)^2$ of Zinc Thiourea sulphate doped TGSP

It gives the Band gap energy for the pureTGSP and Zinc thiourea sulphate doped TGSP. From the study it reveals that the band gap energy for Zinc thiourea sulphate doped TGSP was lower than TGSP. This may be due to the presence of metal ions in the crystal lattice. The cutoff wavelength of pure TGSP is 267nm and ZTS doped TGSP is 278nm.For doped crystals,there is slight shift in wavelength of maximum absorption λmax.This is referred to as bathochromic shift.From this,it is observed that there is change in energy levels to effect transition. The calculated band gap energy and observed band gap energy from Tauc plot for the pure TGSP,Zinc thiourea sulphate doped TGSP is presented in the table.3

Table 3 : Band gap energy for the pure TGSP and Zinc thiourea sulphate doped TGSP

SAMPLES	Tauc plot Eg (eV)	Calculated Eg (eV)
Pure TGSP	4.7	4.65
Zinc thiourea sulphate doped TGSP	4.5	4.46

CONCLUSION

Single crystals of TGSP and semiorganic ZTS doped TGSP were grown by solvent evaporation technique. The crystals grown were of well faceted,highly transparent and bigger in size.Habit modification was observed for the doped crystal.Powder XRD spectrum confirms the crystalline nature and the unit cell volume was slightly increased when compared with TGS and TGSP.Functional groups of the doped TGSP were identified using FTIR spectral analysis.EDX analysis gives the information about the constituent elements in the TGSP and confirms the presence of metal ion Zn^{2+} in the crystal lattice.Habit modification was observed for the doped crystal.Second harmonic generation test was carried out for the powdered ZTS doped TGSP and the relative second harmonic generation efficiency is found to be 2 times greater than KDP.The investigation based on the said characterization and the non- linear efficiency confirm that the ZTS doped TGSP single crystal may be a suitable material for the fabrication of infra ray detectors. Optical absorption studies confirms that the material is a soft material.

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