Growth and Structural Studies of TGS_xP_{1-x} Single Crystals

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Abstract: **TGS_x P_{1-x} binary mixed crystals were grown from an aqueous solution by slow evaporation technique. The grown crystals were characterized structurally and chemically by taking XRD, EDAX, FTIR and measuring the density. The XRD data shown that the mixed crystals belong to monoclinic structure. The lattice parameter calculated obeys both Vegard's law and Retger's rule. The FTIR spectra confirms the functional groups.**

I. INTRODUCTION

Triglycine sulphate (TGS) family single crystals have drawn considerable interest in recent years due to their potential applications in IR detectors, storage devices and laser devices [1]. TGS and phosphate substituted TGS (TGSP) single crystals show a typical second order phase transition at curie temperatures of 49°C and 51°C respectively [2]. TGS family crystals belong to the monoclinic system with the non-polar space group $P2_1$ in the ferroelectric phase and $P2_{1m}$ in the para electric phase. TGS has a wide polarizing b-plane, which is advantageous in device fabrication.

II. MATERIALS AND METHODS

A. Growth procedure

The TGS, TGP and TGSP salts were synthesized from the following reactions.

For TGS

$3(NH_2CH_2\ COOH) + H_2SO_4 \rightarrow (NH_2CH_2COOH)_3 + (H_2SO_4)$

For TGP

$3(NH_2CH_2COOH) + H_3PO_4 \rightarrow (NH_2CH_2COOH)_3(H_3PO_4)$

For TGSP

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

for various values of x viz. 0.2, 0.4, 0.5, 0.6 and 0.8.

Analar grade glycine, sulphuric acid and phosphoric acids were used for the synthesis of respective salts. After successive recrystallisation process, the purified salts were used for the preparation of sugar saturated solution. The super saturated solutions of pure TGS, pure TGP and binary mixed TGSP for various values of x were prepared at 45°C using an optically heated constant temperature bath. Growth was initiated by slow evaporation technique. The crystals were harvested after a typical growth period of two to three weeks.

B. Density and Composition

The density of all the grown crystals were determined by using the floatation technique for quantitative analysis. Bromoform of density 2.890 gm/cc and Ethanol of density 0.789 gm/cc are respectively denser and rarer liquids used. 10ml Ethanol was taken in the test tube and the crystal for which density has to be determined was dropped into it. The crystal was at rest in the bottom of the test tube. Bromoform was then gradually added until the crystal was in a suspended state. Now density of the crystal is equal to the density of the mixed solution. Density of the solution was determined by finding the mass of 10ml of the solution and using the relation.

$$D = \frac{M}{V}$$

where M is the mass of the solution and V is the volume of the solution. The density is equal to the density of the crystal. The composition of all the mixed crystals were determined from the measured density values using the relation

$$d = xd_1 + (1-x)d_2$$

where d is the density of the mixed crystal, d_1 and d_2 are the densities of TGP and TGS respectively.

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FTIR and EDAX

FTIR and EDAX spectra were taken to confirm the presence of the components.

Lattice Parameter

Powder X-ray diffraction data were collected using XPERT-PRO Diffractometer, using CUK∝, (1.5406)A° wavelength.

III. RESULTS AND DISCUSSION

The photograph of all the grown crystals are shown in fig.1. It is found that the grown crystals are transparent, stable and optically good quality crystal. The maximum size of the crystal obtained is 18×20×5mm.

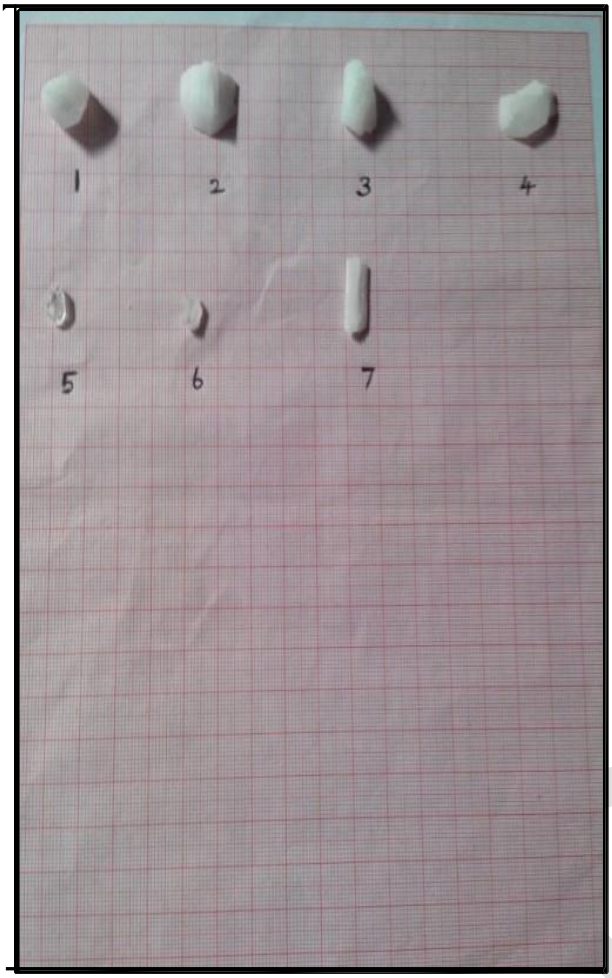

Fig.1. Photograph of all grown crystals

The density and the estimated composition of all the grown mixed crystals are given in Table 1. The estimated composition of all the mixed crystals agreed with the actual composition taken.

Table 1. Values of Density and Estimated Composition of all the Grown Crystals

System	Density (gm / cc)	Estimated Composition
TGS_{pure}	1.705	-
TGS_{pure}	1.478	-
TGSP	-	- $TGS_{0.177}$ $P_{0.82}$
$TGS_{0.2}P_{0.8}$	1.66	$TGS_{0.41}P_{0.59}$
$TGS_{0.4}P_{0.6}$	1.613	$TGS_{0.46}P_{0.538}$
$TGS_{0.5}P_{0.5}$	1.35	$TGS_{0.6}P_{0.4}$
$TGS_{0.6}P_{0.4}$	1.57	$TGS_{0.746}P_{0.25}$
$TGS_{0.8}P_{0.2}$	1.53	

The wave number assigned to the functional groups for TGS0.5 P0.5 crystal is given in Table 2. It is found that all the fundamental functional groups in the raw materials are present in the mixed crystals also. The FTIR spectrum of TGS0.5 P0.5 crystal is given in fig.2 for illustration.

The NH, OH and CH absorptions are smeared in to a Continuum, which occur at a high frequency 3106 cm-1. The frequency assigned for COO- stretching is
1505 cm-1. The absorbtion in the range 2110 - 2220 assigned for CH stretching for
COO group. The strong absorbtion in the range 1126 - 1153 cm-1 is evidently due to the sulphate part of the molecule. The broad band around 1126 cm-1 is assigned to - C - N asymmetric stretch of both SO4 and PO4 which lies in the same envelope of C - N stretch. The frequencies obtained at 1234cm-1 and 685 cm-1 corresponds to sulfate part of the ions. The frequency obtained at 1043 cm-1 corresponds to phosphate ions.

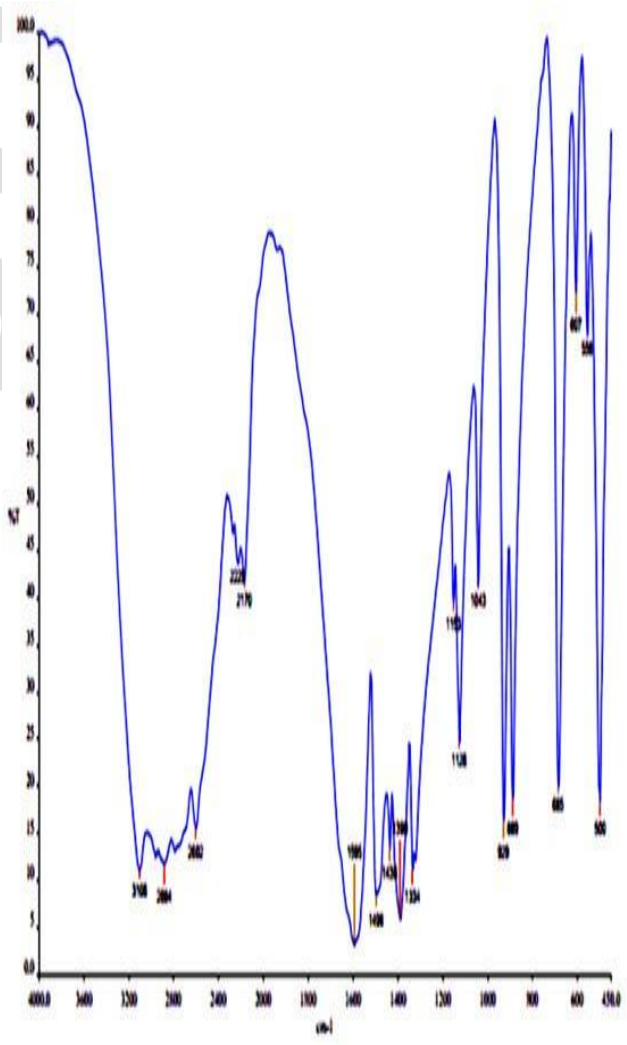

Fig.2. The FTIR spectrum of TGS0.5 P0.5 crystal

Table 2. Vibrational Assignments for the functional groups for $TGS_{0.5}P_{0.5}$ crystal

Frequency (cm^{-1})	Assigned functional group
3106	NH, OH and CH absorptions
2884	NH_2 stretching / CH_2 stretching
2602	NH_2 stretching
2220	COO^- asymmetrical stretching
2110	COO^- asymmetrical stretching
1505	COO^- stretching
1498	COO^- stretching
1438	OCH, CH_2 bending
1396	CO - stretching
1234	Sulfate ions
1153	C - O stretching / C - C stretching / COH bending asymmetry structure of SO_4 and PO_4
1126	C - N stretching C - N asymmetry stretch of SO_4 and PO_4
1043	Phosphate ions
920	CH_2 rocking
882	CH_2 deformation
685	COO^- bending
607	COO^- wagging
556	CS stretching
500	COO^- rocking

The XRD pattern of $TGS_{0.5}P_{0.5}$ is shown in fig. 3. The calculated lattice parameter are given in Table 3. The calculated lattice parameter shows that all the grown crystals belong to monoclinic system. The lattice parameter of pure TGS [3] and $TGS_{0.5}P_{0.5}$ [4] agreed with the literature value. The lattice parameters of the mixed crystals were estimated by using Vegards law and Retgers rule.

The Vegards law [5] is

$$a = xa_1 + (1 - x)\, a_2$$
$$b = xb_1 + (1 - x)\, b_2$$
$$c = xc_1 + (1 - x)\, c_2$$

Retgers rule [6] is

$$a^3 = xa_1^3 + (1 - x)\, a_2^3$$
$$b^3 = xb_1^3 + (1 - x)\, b_2^3$$
$$c^3 = xc_1^3 + (1 - x)\, c_2^3$$

The estimated values are given in Table 3.

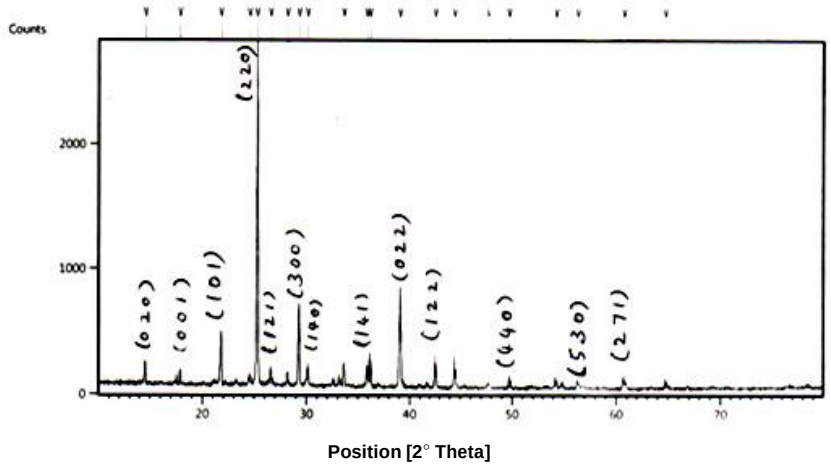

Fig. 3. The XRD pattern of $TGS_{0.5}$ $P_{0.5}$

Table 3. Values of Calculated and Estimated Lattice Parameters

System	Calculated			Lattice Parameters Estimated Vegards law			Retgers rule			β
	a	b	c	a	b	c	a	b	c	
TGS_{pure}	9.3789 (9.38)	12.7177 (12.634)	5.4855 (5.734)							110° (109° 55')
TGP_{pure}	9.758	12.656	5.331							110°
TGSP										
$TGS_{0.2}$ $P_{0.8}$	9.732	12.457	5.320	9.682	12.668	5.362	9.683	12.668	5.363	110°
$TGS_{0.4}$ $P_{0.6}$	9.752	12.243	5.329	9.606	12.680	5.393	9.610	12.680	5.394	110°
$TGS_{0.5}$ $P_{0.5}$	9.734 (9.150)	12.573 (12.690)	5.272 (5.734)	9.568	12.686	5.408	9.572	12.687	5.409	110°
$TGS_{0.6}$ $P_{0.4}$	9.555	12.712	5.405	9.530	12.693	5.423	9.534	12.693	5.424	110°
$TGS_{0.8}$ $P_{0.2}$	9.733	12.662	5.385	9.454	12.705	5.454	9.457	12.705	5.455	110°

IV. CONCLUSION

The crystals grown in the presence study are mixed single crystals which are more stable and transparent. The crystals crystalized in monoclinic structure and the lattice parameters of the mixed crystals agreed with those calculated from Vegards and Retgers rule.

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