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Growth and Characterization of Triglycine Sulphate Crystal

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I. Introduction

Tri Glycine Sulphate (TGS) is a well known ferroelectric and pyroelectric material below its critical temperature (49^oC) [1]. It finds application in the fabrication of infrared detectors, pyroelectric vidicon tube operating at room temperature, in the fabrication of capacitors, transducers and sensors [2-3]. TGS belongs to the biaxial monoclinic system associated with the polar space group $P2_1$ in the ferroelectric phase and it crystallizes in $P2_1/m$ space group in the paraelectric phase [4-6] . The monoclinic b-axis is known to be parallel to spontaneous polarization direction. Therefore the b-cut (010) crystals are technologically important for many device applications [7-9]. Ferro electric TGS exhibits antiparallel 180^o domains, generally parallel to b-axis. The domains in the majority of the crystals are rod shaped, with lenticular cross sections elongated in the direction perpendicular to the crystallographic c-axis [10]. It was first demonstrated by Le Bihan by scanning electron microscopy technique [11]. The two hydrogen atoms of sulphuric acid of TGS are protonated to the carboxylic group of two zwitterionic molecules, and the carboxylic hydrogen atom combined with the amino group of the third glycine molecule and forms a zwitterions [12]. TGS has some disadvantages such as,

i. Ferroelectric Domains Possess High Mobility At Room Temperature
ii. Easy Depolarization By Electrical, Mechanical And Thermal Means
iii. Microbial contamination during the growth time [13-15].

The characterization studies on TGS crystal [16-18] with dopants such as L-alanine [19], Sodium Bromide [20], Magnesium Chloride [21], Calcium [22], Potassium Bromide [23], Ammonium dihydrogen Phosphate [24], Ammonium Chloride [25], Lithium Sulphate [26], Quanidine [27], rare earth elements [28], Chromium [29], Phosphoric acid [30], L-tyrosine [31], L-Cystine [32], Palladium [33], L-Threonine [34], urea [35], DL-methionine [36], EDTA [37] and DL-Phenyl alanine [38] have been already reported.

In the present study, TGS crystal has been grown by the conventional slow evaporation method. The main objective of the present work is to investigate the effect of the structural, vibrational and mechanical properties of TGS crystals.

II. Crystal Growth

The single crystal of Tri Glycine Sulphate has been synthesized by dissolving Glycine and Sulphuric acid in a molar ratio of 3:1 in deionized water. The chemical reaction performs as follows,

$3\,(NH_2CH_2COOH) + H_2SO_4 \,®\, (NH_2\,CH_2\,COOH)_3\,(H_2SO_4)$ (1)

A saturated solution was prepared by stirring 8 hours continuously and filtered using whatman filter paper. The solution was allowed for slow evaporation by keeping it in the dust free atmosphere. After three weeks, well transparent, colourless crystals have been harvested. The photograph of the grown TGS crystal is shown in Fig.1.

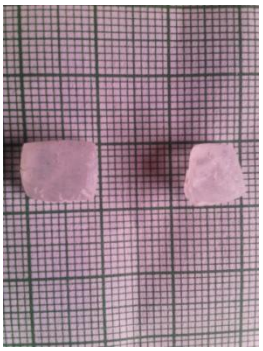

Fig.1 Photograph of the grown TGS crystal

III. Material characterization

The grown TGS crystals were subjected to powder x-ray diffraction studies using SEIFERT diffractometer at room temperature with CuKα radiation of wave length (λ=1.5406 Å) to confirm the identity of the grown crystal. The single crystal XRD study of TGS crystal was carried out using ENRAF NONIUS CAD4-F single crystal x-ray diffractometer with Mokα (λ=0.7170Å) radiation. The FTIR spectrum of TGS crystal was recorded in the region 400-4000cm^{-1} at a resolution of ±2cm^{-1} using Perkin Elmer Spectrophotometer. Hardness of the grown TGS crystal was measured using Leitz – Wetzler hardness tester fitted with a Vickers diamond pyramidal indenter. Indentations were made for various loads from 25g to 100g, the average diagonal lengths were measured for a regular interval of 10 seconds.

IV. X-ray diffraction analysis

The indexed powder x-ray diffraction pattern for TGS crystal is depicted in Fig. 2. The sharp peaks confirmed the crystalline nature. From single crystal XRD studies it is found that the grown TGS crystal crystallized in monoclinic system with lattice parameters a=5.732 Å, b=12.631Å, c=9.163Å, β=105.52Å and V=639.1Å^3.

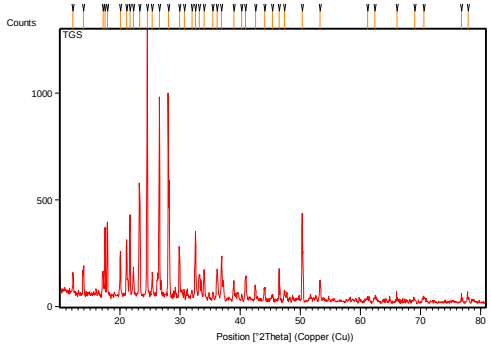

Fig.2 Powder XRD pattern of the grown TGS crystal

V. FTIR Analysis

The recorded FTIR spectrum of pure TGS crystal is shown in Fig.3. The band at 3423cm^{-1} is assigned to antisymmetric NH_3^+ stretching. The peaks appeared at 3169 and 3009 cm^{-1} is attributed to symmetric stretching of NH_3^+. In the region between 2500 and 3400 cm^{-1}, the OH stretching of carboxyl group, NH stretching and aliphatic CH stretching overlap together. The CH_2 stretching mode is observed at 2911cm^{-1}. The peaks at 2705 and 2611cm^{-1} are due to NH_3^+ overtones and combination bands. The C=O stretching of COOH group is observed at 1596 cm^{-1}. The bending mode due to NH_3^+ are clearly seen at 1517 cm^{-1}. The CH_2 bending appear at 1398 cm^{-1}. The asymmetric stretching mode of sulphur appear at 1293 cm^{-1}. The peak appear at 1123 cm^{-1} is associated with C-N stretching. The peaks at 901, 811 cm^{-1} strongly suggest the presence of C-C stretching mode. The peaks at 764, 680, 618, 508 cm^{-1} corresponds to NH_3^+ for torsional oscillations. FTIR intensity and frequencies of the grown TGS crystal matches with the reported literature [39]. The FTIR assignments of the grown TGS crystal are given in Table.1

Table. 1 FTIR Assignments of the grown TGS crystal

Wave number (cm^{-1}) observed	**Wave number (cm^{-1}) Reported [21, 34, 39]**	**Assignments**
3423	3405	$(NH_3)^+$ anti symmetric stretching
3169	3173	$(NH_3)^+$ symmetric stretching
3009	2914	CH_2 stretching
2911		
2611	2636	NH_3+ overtones and combination bands
2705	2783	
1596	1568	C-O stretching of COOH group
1517	1518	$(NH_3)^+$ anti sym. bending
1398	1329	CH_2 bending
1291	1309	S=O asymmetric stretching
1123	1118	C-N stretching
901	901	C-C stretching
811		

680	669	NH_3^+ torsional oscillation
618	615	C_2 out of Plane bending $+C_2N$ torsion $+C_{10}$ out of plane bending
508	500	C_1N torsion + N_2H out of Plane bending

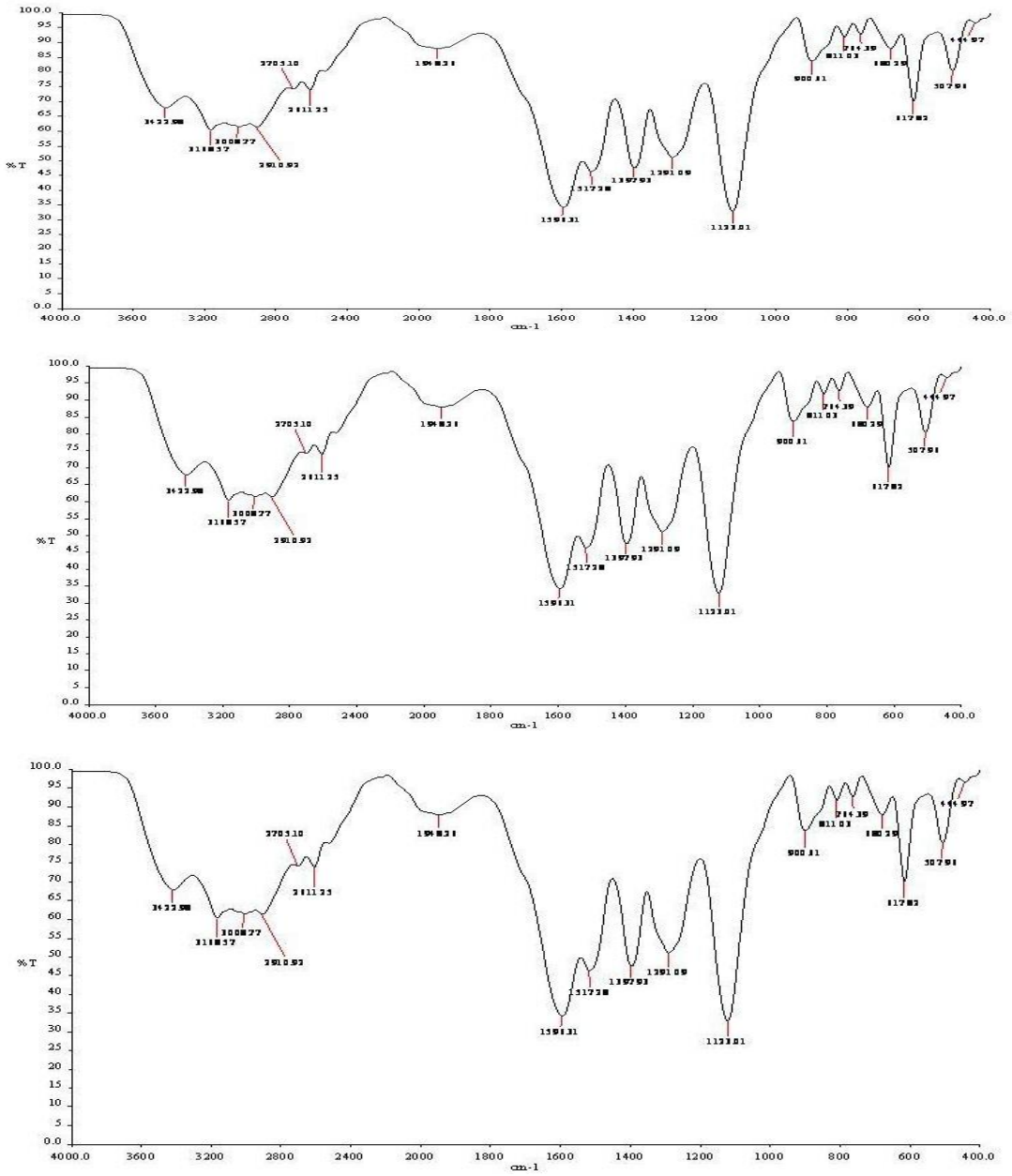

Fig. 3 FTIR spectrum of the grown TGS crystal

VI. Micro hardness Analysis

Hardness of a material is a measure of resistance, that offers to deformation. The Vicker's hardness value (H_V) was found out from the relation,

$$H_v = 1.8544 \frac{P}{d^2} \text{ Kg/mm}^2 \qquad (2)$$

Where P is the applied load and d is the average diagonal length [40]. The variation of microhardness with the applied load is shown in Fig.3.4.

It is evident from the plot that the Vickers hardness number increases with increasing applied load, thus it exhibit reverse indentation size effect (RISE). At low loads nucleation of dislocations formed along the particular slip system, but with increasing load, dislocation multiplication extends to other inner layers also.

Above 100 gm, cracks were developed on the smooth surface of the crystal due to the release of internal stresses generated locally of indentation. According to Meyer's law [41],

$P = K_1 d^n$ ® (3)

$\log P = \log K_1 + n \log d$. (4)

Where P is the applied load, d is the diagonal length of indentation, K_1 is the standard hardness and n is the work hardening co-efficient has been found out using the slope of log d vs log P plot (Fig.3.5).

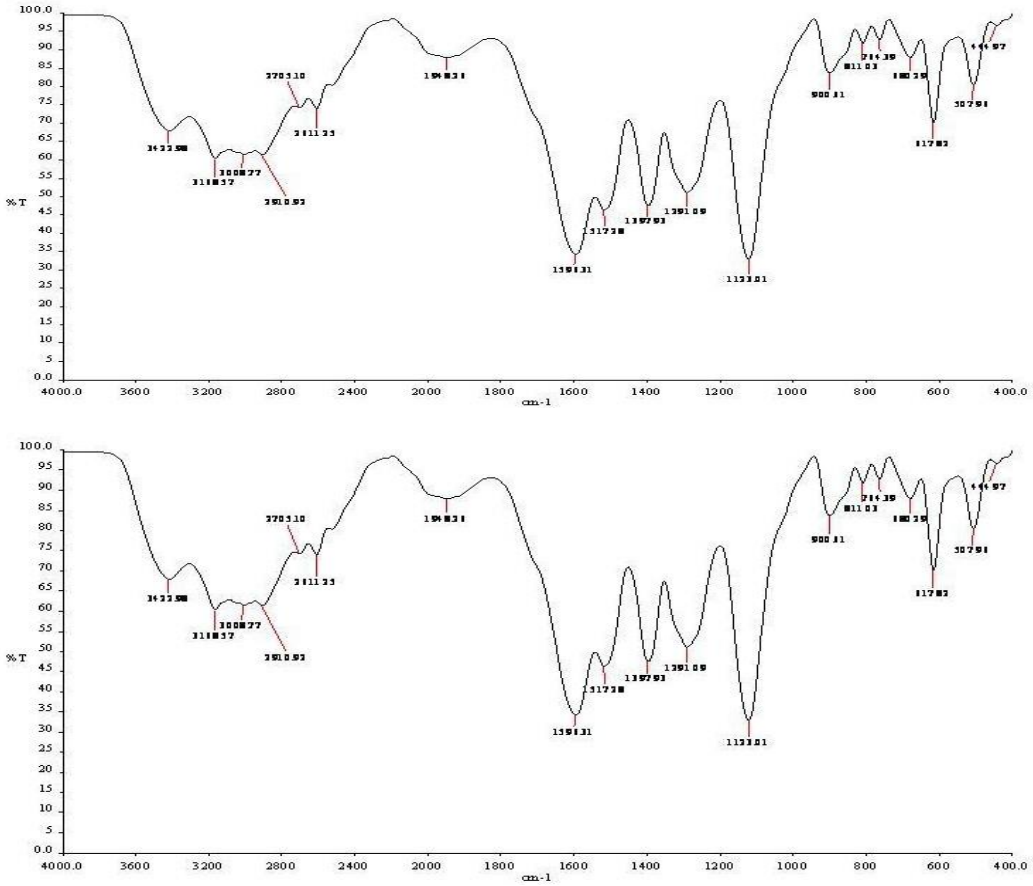

Fig.4 Variation of microhardness value with the applied load

From careful observation on different materials, Onitsch [42] pointed out that n lies between 1 and 1.6 for moderately hard materials, and it is more than 1.6 for soft materias. In the present study, the value of n is 2.76, suggest that the grown TGS crystal belongs to soft material category. The yield strength (σ_v) is determined using the relation [43],

$\sigma_v = H_v/_{2.9} \{[1-(n-2)] \times [12.5 (n-2)/_{1-(n-2)}]^{n-2}\}$

The yield strength of the grown TGS crystal has been estimated as87.80 MPa.

VII. Conclusion

The Triglycine sulfate (TGS) crystal has been grown by the conventional slow evaporation technique. Its identity was confirmed by powder XRD technique. It is crystallized in monoclinic system with space group P21/m with lattice parameters a=5.732Å, b=12.631Å, c=9.163Å, β=105.52Å. The grown crystal exhibit reverse indentation size effect. Micro hardening coefficient determines that it belongs to soft material category.

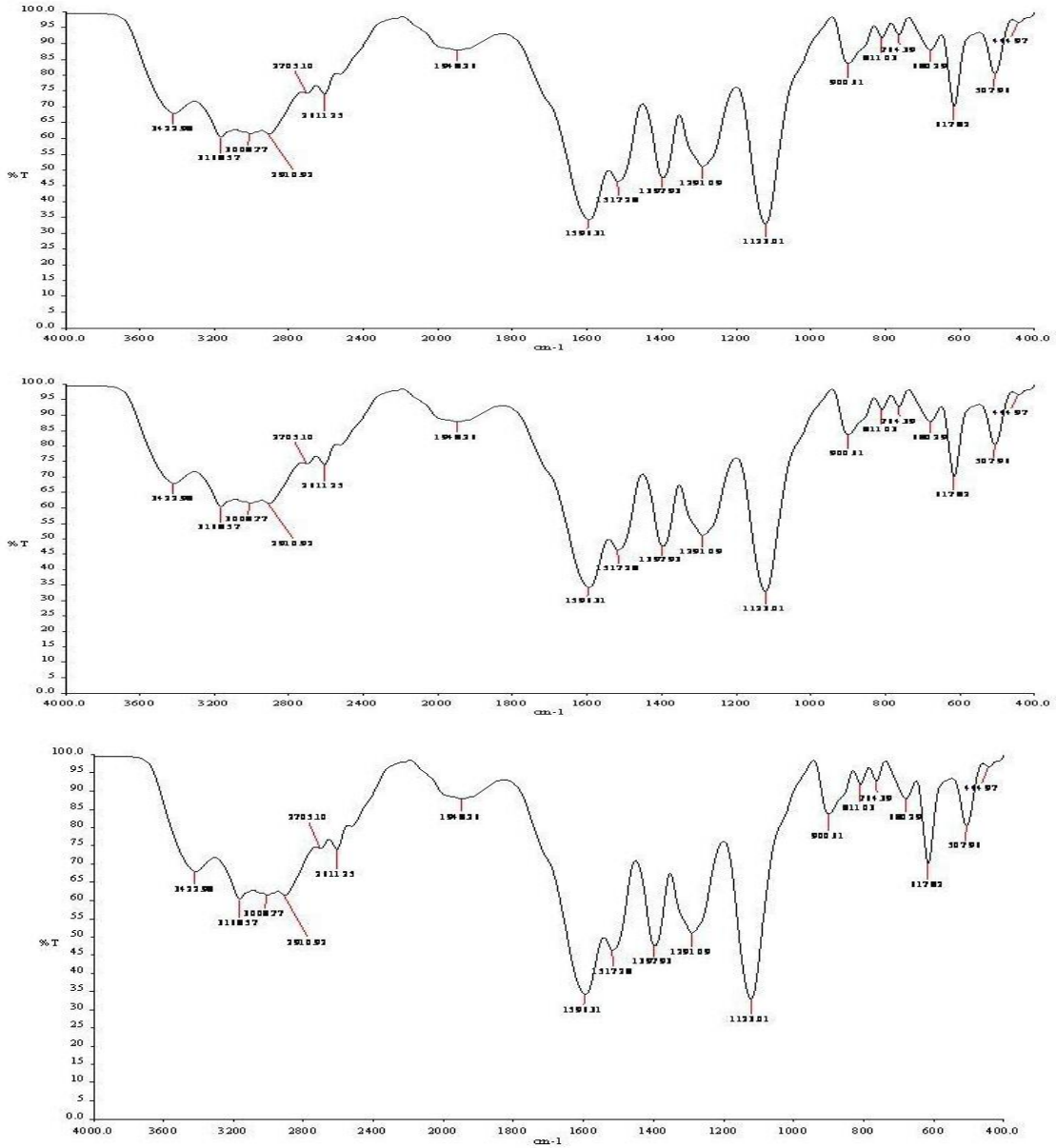

Fig.5 log P Vs log d plot for the grown TGS crystal

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