

Vibrational Spectroscopic Studies on Amino acid Doped TGS Single Crystals: An Experimental and Theoretical Approach

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Abstract— Single crystals of pure Triglycine sulphate (TGS), L-asparagine doped TGS (LATGS) and L-glutamine doped TGS (LGTGS) were grown by the slow evaporation method. The structural characterization was carried out by single crystal XRD technique and found that all the grown crystals crystallize in monoclinic structure. Fourier transform infrared and Raman spectra were recorded and analyzed. The line broadening was observed for L-asparagine doped TGS and L-glutamine doped TGS crystals. The broadening of the spectral line is due to the dopant molecules, which are bigger in size than the glycine molecule. The density functional theory (DFT) method was performed using Gaussian 09 software for obtaining the vibrational wave numbers. The FTIR and Raman spectra were simulated and visualized by using Gauss View 5. A comparison between theoretical frequencies of glycinium ion, glycine zwitter ionic form and experimentally observed FTIR and Raman modes for pure TGS and amino acid doped TGS crystals were discussed. The experimental results agree well with the theoretical results.

Keywords: Amino acid, DFT method, FTIR, line broadening, optimized structure, Raman, Vibrational modes,

1 INTRODUCTION

CRYSTALS of Triglycine sulphate (TGS), is a well-known ferroelectric crystal of infrared detection applications mainly because of its features which allow operation at room temperature and without external bias voltage [1,2]. The ferroelectric nature of triglycine sulphate was discovered by Matthias *et al* [3]. The crystal structure of TGS was reported by Hoshino *et al* [4]. TGS is one of the very few ferroelectrics known to exhibit a second-order phase transition and hence offers possibilities for the observation of genuine critical phenomenon very close to the Curie temperature. The spontaneous polarization of ferroelectric crystal originates from the dipole moment of each dipole within the crystal. Some molecules with high dipole moments can be introduced into the polar lattice of a TGS crystal in such a way that their polar orientation tends to coincide with that of bulk polarization. Thus the pyroelectric properties of the crystal can be improved. The ferroelectric TGS single crystals are considered as a potential material for infrared (IR) detection by virtue of their high pyroelectric coefficient and low dielectric constant [5]. Single crystals of TGS are considered to be the most suitable materials for environmental analysis monitors, earth observation cameras, astronomical telescopes, military systems and target faces vidicons based on the pyroelectric effect. However, the tendency of the crystals to depolarize with time is a serious drawback [6]. Numerous studies have been reported on the minimization of the depolarization effects, and a number of organic, inorganic, metallic as well as rare earth ions have been introduced as dopants [7-10]. An efficient way to stabilize the single domain state is practiced by doping an optically

active molecule into TGS. In triglycine sulphate, glycine is one of the amino acids, which contains no asymmetric carbon atoms belongs to the class of hydrocarbon. Glycine molecule causes an internal bias field, which causes the crystal permanently depolarized. The substitution of another amino acid, for glycine has been found to improve the crystal properties by contributing to the effective internal bias in these crystals. This in turn prevents the depolarization-with-time phenomenon, thereby giving a permanently poled single domain crystal. The hardness of the amino acid doped crystal may be expected to be low as compared to the pure TGS crystal. Thermal stability may be increased due to the incorporation of amino acids in pure TGS. Vibrational spectroscopy is an efficient tool for the characterization of crystalline materials. It is effectively used to identify functional groups and determining the molecular structure of synthesized crystals. In the present work, we report the synthesis, structural characterization, FTIR, Raman and DFT studies of pure Triglycine sulphate (TGS), L-asparagine doped TGS (LATGS) and L-glutamine doped TGS (LGTGS).

2 EXPERIMENTAL DETAILS

TGS is synthesized using AR grade glycine ($\text{NH}_2\text{CH}_2\text{COOH}$) and sulphuric acid (H_2SO_4) in slow evaporation method. In order to prepare TGS solution, glycine is dissolved in sulphuric acid in the ratio 3:1. The impurity content of the TGS solution is minimized by re-crystallization for 3 times. A saturated solution of TGS at 40°C is prepared using recrystallized salt. The 0.5 mol% of dopants (amino acids) is added to the saturated TGS solution. The solution is filtered using a sintered glass filter, a high quality cat no.1001 125 Whatman filter paper. The filtered solution is kept for slow evaporation at room temperature. The grown crystals were harvested in 21

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days. The prepared samples are transparent and free from any noticeable defects.

2.2 Raman Measurements

Raman spectral measurements were carried out using Bruker IFS 66v FTIR spectrometer attached with FRA 106 Raman module. The Raman spectra were recorded in the region 400-3500 cm⁻¹. This instrument has a resolution of 0.1 cm⁻¹. The source of excitation used here is Nd-YAG Laser (1064 nm).

2.3 Infrared Measurements

The FTIR spectra is recorded in the region 400-3500 cm⁻¹ in evacuation mode on Bruker IFS 64V spectrophotometer using KBr pellet technique (solid phase) with 4.0 cm⁻¹ resolutions.

3 RESULTS AND DISCUSSION

3.1 X-ray diffraction studies

The grown crystals were subjected to single crystal X-ray diffraction analysis to find the lattice parameters. The single crystal X-ray diffraction study reveals that there is a significant change in the lattice parameter due to the incorporation of dopant into the crystal lattice. Table (1) shows the Lattice parameters of TGS and amino acid doped TGS single crystals.

TABLE 1
LATTICE PARAMETERS

Crystal	a (Å)	b (Å)	c (Å)	β (deg)	Unit cell Volume (Å ³)
TGS	5.712	12.561	9.119	105.69	630.2
LATGS	5.725	12.605	9.150	105.65	641.6
LGTGS	5.710	12.622	9.156	105.66	635

Å = armstrong, deg = degree

This indicates that all the crystals belongs to the monoclinic system. The lattice parameters (b and c) of LATGS and LGTGS crystals are found to be slightly higher than those observed in pure TGS. The slight increase in lattice parameter and volume of the unit cell of the LATGS and LGTGS crystals are attributed to the replacement of smaller lattice glycine molecules by the larger L-asparagine and L-glutamine molecules, and the lattice could be strained.

3.2 FTIR and FT-Raman analyses

In this work, the FTIR and Raman vibrational frequencies of pure TGS and amino acid doped TGS crystals were assigned on the basis of normal coordinate analysis. The recorded FTIR and Raman spectra are depicted in Figs. 1 and 2 respectively.

Theoretical vibrations of Glycine and Glycine ions are compared with experimental Raman and FTIR vibrations of TGS

S.No	Theoretical vibrations		Experimental vibrations		Assignments
	Wavenumber (cm ⁻¹)		Wavenumber (cm ⁻¹)		
	Glycine (Zwitter ion)	Glycine ion	TGS (Raman)	TGS (FTIR)	
1	494	500	464(mb)	499 (vs)	COO ⁻ rocking
2	544	558	584(m)	570 (vs)	NH ₃ ⁺ torsion
3	-	-	617	617 (vs)	SO ₄ ²⁻ bending / COO ⁻ wagging
4	654	-	658(mb)	-	COO ⁻ scissoring
5	786	789	-	-	NH ₃ ⁺ asymmetric bending
6	868	839	892(s)	860 (s)	C-CN ⁺ stretching/ NH ₃ ⁺ rocking
7	910	907	-	903 (vs)	NH ₃ ⁺ rocking/ SO ₄ ²⁻ symmetrical stretching
8	-	959	985(vs)	977 (w)	CH ₂ twisting / SO ₄ ²⁻ symmetrical stretching
9	-	1018	-	1018(w)	CN stretching
10	1043	-	1047(mb)	1055 (vw)	CN stretching
11	1077	1079	-	1084(w)	NH ₂ bending
12	-	-	1115(mb)	1128(m)	NH ₃ ⁺ rocking/ SO ₄ ²⁻ out of plane stretching
13	1184	1189	-	-	NH ₂ twisting
14	-	1303	-	1303(s)	CH ₂ wagging
15	1345	1350	-	-	CH ₂ wagging
16	1355	1392	1302(s)	1379(s)	CH ₂ bending
17	1485	1481	-	1427(vs)	COO ⁻ symmetrical stretching/ SO ₄ ²⁻ asymmetric stretching
18	1512	1557	-	1500(vs)	Symmetric NH bending
19	-	-	1611 (mb)	1620(vs)	COO ⁻ asymmetrical stretching
20	1709	1704	-	1710	NH ₃ ⁺ deformation
21	1818	-	-	1865(sh)	C-O stretching
22	-	-	2993(s)	-	NH stretching of NH ₃ ⁺
23	2788	-	-	-	NH stretching
24	-	3006	3020(w)	-	Symmetrical C-H stretching
25	-	3010	-	-	CH ₂ symmetric stretching
26	3090	3072	-	-	CH ₂ symmetric stretching
27	3137	-	3165(mb)	3165(mb)	NH ₃ ⁺ symmetric stretching
28	3440	3417	3480(w)	-	NH ₂ symmetric stretching
29	-	3510	-	-	NH ₂ asymmetric stretching

The observed wavenumbers, relative intensities obtained from

TABLE 2

the experimental and simulated spectra are found to be in good agreement with the reported literature [11]. The theoretical IR and Raman vibrations for glycinium ion and glycine zwitter ionic form were obtained by DFT method using the basis set 6-21G. A comparison between theoretical frequencies of glycinium ion, glycine zwitter ionic form and observed FTIR and Raman modes for pure TGS and amino acid doped TGS crystals were discussed. Table 2 and Table 3 shows the FTIR and Raman assignments for pure and amino acid doped TGS crystals.

3.3 NH₃ Vibrations

All the spectra give NH₃⁺ group vibrations, it shows the zwitterion configuration of amino acids. All these crystals exist as a dipolar (zwitter) ions in the crystalline state. The position of the NH stretching bands was observed at high frequency regions, which indicates that the formation of fairly strong hydrogen bonding. The broad absorption near 3167 cm⁻¹ was observed in the Raman and FTIR spectra of pure and amino acid doped TGS crystals [12].

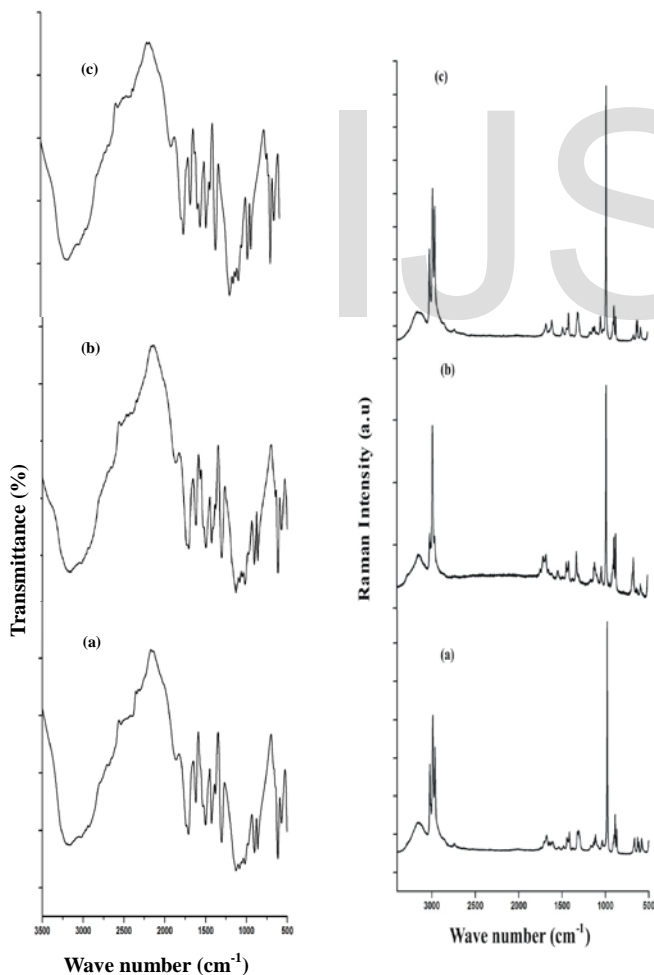


Fig. 1. FTIR spectra of (a) pure TGS (b) LATGS and (c) LGTGS

Fig. 2. Raman spectra of (a) pure TGS (b) LATGS and (c) LGTGS

TABLE 3

Experimental Raman and FTIR vibrations of LATGS and

LGTS

S.No	Experimental vibrations Wavenumber (cm ⁻¹)				Assignments
	Raman		FTIR		
	LATGS	LGTS	LATGS	LGTS	
1	453(mb)	453	499 (vs)	499	COO ⁻ rocking
2	580(w)	-	570 (vs)	570	NH ₃ ⁺ torsion
3	631	615	615	617	SO ₄ ²⁻ bending / COO ⁻ wagging
4	670	670	646(m)	669	COO ⁻ scissoring
5	890(s)	890(s)	862(s)	860	C-CN ⁺ stretching
6	-	-	902 (vs)	904	NH ₃ ⁺ rocking /
7	978(vs)	980	974(w)	972	CH ₂ twisting / SO ₄ ²⁻ symmetrical stretch- ing
8	-	-	1018(w)	1020	CN stretching
9	1114(vw)	1044	1051(w)	1053	CN stretching
10	-	-	1085(w)	1084	NH ₂ bending
11	1136(w)	1132	1130	1130	NH ₃ ⁺ rocking/ SO ₄ ²⁻ Out of plane stretch- ing
12	-	-	1303(s)	1303	CH ₂ wagging
13	-	-	-	-	CH ₂ wagging
14	1315(mb)	1310(mb)	1377(s)	1377	CH ₂ bending
15	-	-	1427(vs)	1427	COO ⁻ symmetrical stretching/ SO ₄ ²⁻ asymmetric stretching
16	-	-	1500(s)	1500(s)	Symmetric NH bend- ing
17	-	-	1620(s)	1622	COO ⁻ asymmetrical stretching
18	1675(mb)	1684(mb)	1734(m)	1749	C=O stretching
19	-	-	1867	1867	C-O stretching
20	-	-	2157(w)	2147	NH stretching of NH ₃ ⁺
21	2651	2649	2342(w)	-	-
22	-	2982	-	-	"
23	2993(s)	2990(s)	2534(w)	2530	"
24	2995	-	2645	-	NH stretching
25	3027(w)	3027(mb)	-	-	Symmetrical C-H stretching
26	-	-	3022	-	CH ₂ symmetric stretching
27	3160	3162	3163(m)	3167	NH ₃ ⁺ symmetric stretching

The bending vibrations of the NH₃⁺ group were appeared at 1500 cm⁻¹ in FTIR spectra of pure and amino acid doped TGS crystals. This mode was not visible in the Raman spectra. The NH₃⁺ rocking vibrations were observed around 903 and 890 cm⁻¹ in the FTIR and Raman spectra respectively.

3.4 The stretching vibrations of the COO⁻ group

Amino acids usually exist as zwitterionic form in

crystals. They have an ionized carboxyl group (COO⁻) and the amine salt NH₃⁺. The infra red peaks were observed at 1620 and 1427 cm⁻¹ and assigned for the asymmetric and the symmetric vibrations of COO⁻ respectively, which indicate the presence of a zwitter ionic form. The COO⁻ asymmetric stretching was observed around 1611 cm⁻¹ in Raman spectra of pure TGS [13] and the same Raman band was observed around ~1620 cm⁻¹ for amino acid doped TGS crystals.

3.5 Carboxyl vibrations

The carboxyl C=O stretching wavenumbers can easily be recognized in FTIR and Raman spectra. Aminoacids in cationic form depending on the strength of interaction are expected to give a band around 1700 cm⁻¹ due to stretching motion of C=O atoms. The medium narrow band was obtained around 1734 cm⁻¹ and assigned to C=O stretching, which indicates the presence of glycine molecule [14]. This band was obtained with weak intensity at 1675 cm⁻¹ in Raman spectra of amino acid doped TGS crystals.

3.6 Vibrational modes of SO₄²⁻

The vibrational modes of SO₄²⁻ ion were listed in Table 2 and Table 3. The vibrational modes of SO₄²⁻ were identified and assigned in all the three systems. The SO₄²⁻ bending mode and symmetrical stretching vibrations were observed ~620 and ~980 cm⁻¹ for pure and amino acid doped TGS in both FTIR and Raman spectra respectively. The Raman and FTIR spectra shows SO₄²⁻ out of plane stretching vibrations around 1120 cm⁻¹ for pure TGS. The same vibrational mode was observed ~1130 cm⁻¹ for amino acid doped TGS crystal in both FTIR and Raman spectra. The SO₄²⁻ asymmetric stretching vibration was observed at 1427 cm⁻¹ as a very strong peak in the FTIR spectra of pure and amino acid doped TGS crystals.

4 CONCLUSION

The Single crystals of pure Triglycine sulphate (TGS), L-asparagine doped TGS (LATGS) and L-glutamine doped TGS (LGTGS) were grown by the slow evaporation method and characterized by XRD, FTIR and FT-Raman Spectroscopic techniques. The structural characterization was carried out by single crystal XRD technique and found that all the grown crystals crystallize in monoclinic structure. The density functional theory (DFT) method was performed using Gaussian 09 software for obtaining the vibrational wave numbers. The FTIR and Raman spectra were simulated and visualized by using Gauss View 5. A comparison between theoretical frequencies of glycinium ion, glycine zwitter ionic form and experimentally observed FTIR and Raman modes for pure TGS and amino acid doped TGS crystals were discussed. The experimental results agree well with the theoretical results. The NH₃ vibrations, the stretching vibrations of the COO⁻, carboxyl vibrations, vibrational modes of SO₄²⁻ were identified and assigned for the pure and amino acid doped TGS crystals. The

line broadening was observed for L-asparagine doped TGS and L-glutamine doped TGS crystals. The broadening of the spectral line is due to the dopant molecules, which are bigger in size than the glycine molecule.

5 ACKNOWLEDGEMENTS

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REFERENCES

- [1] Mohan Kumar, R.; Rajan Babu, D.; Jayaraman, D.; Jayavel, R.; Kitamura, K. J. *Cryst. Growth* (2005) 275, 1935.
- [2] Whatmore R W 1986 *Rep. Prog. Phys.* **49** 1335
- [3] B. T. Matthias, C. E. Miller and J. P. Remeika, *Phys. Rev.* **104** (1956) 849-50.
- [4] Hoshino S Okaya Y and Pepinsky R 1959 *Phys. Rev.* **115** 323
- [5] Arunmozhi G Jayavel R and Subramanian C 1998 *Mat. Lett.* **33** 251
- [6] Novotny J Prokopova L and Micka Z 2001 *J. Cryst. Growth*, **226** 333
- [7] Sun X Wang M Pan Q W Shi W and Fang C S 1999 *Crystal. Res. Technol.* **34** 1257-1254
- [8] Meera K Muralidharan R Santhanaraghavan P Gopalakrishnan R and Ramasamy P 2001 *J. Crystal Growth* **226** 312
- [9] Aravazhi S Caravel R and Subramanian C 1997 *Materials Research Bulletin*, **32** 1503-1513
- [10] Guangyong Zhu, Xian Zhu
- [11] , Qi Fan, Xueliang Wan, *Spectrochimica Acta Part A* **78** (2011) 1187-1195
- [12] J. Michalski, E. Kucharska, W. Sasiadek, J. Lorenc, J. Hanuza, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **112**, (2013) 263-275.
- [13] E. Kucharska, J. Michalski, W. Sasiadek, Z. Talik, I. Bryndal, J. Hanuza, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **107**, (2013) 317-325.
- [14] V. Krishnakumar, S. Sivakumar, R. Nagalakshmi, S. Bhuvanewari and M. Rajabopathi, *Spectrochimica Acta Part A* **71** (2008) 480-485.
- [15] R. Parimaladevi, C. Sekar, V. Krishnakumar, *Spectrochimica Acta Part A* **75** (2010) 617-623.