

# Vibrational Spectral Studies of Pure and Doped DTGS Crystals

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**Abstract** Single crystals of deuterated triglycine sulfate (DTGS), DTGS doped with deuterated phosphoric acid (DTGS<sub>(0.8)</sub>P<sub>(0.2)</sub>) [DTGSP], and L-alanine (DTGS<sub>(0.8)</sub>P<sub>(0.2)</sub>—LA<sub>(2 gm)</sub>) [DTGSP-LA] are grown from deuterated water solution containing glycine, D<sub>2</sub>SO<sub>4</sub>, D<sub>3</sub>PO<sub>4</sub>, and L-alanine. Vibrational spectroscopic analysis has been undertaken to examine the configuration of glycinium ion formation and the changes in the nature of hydrogen bonding due to the partial substitution of SO<sub>4</sub><sup>2-</sup> by PO<sub>4</sub><sup>3-</sup>. Fourier Transform Infrared (FT-IR) and FT-Raman analysis indicates the presence of both zwitter and glycinium ions in the doped DTGS crystals, which is due to the low incorporation of dopants into the crystal lattice, which supports Hoshino's theory of spontaneous polarization reversal. Nuclear magnetic resonance studies (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P) revealed the possible bond formation during the formation of the compound.

**Keywords** Ferroelectric crystal, Infrared spectroscopy, Raman spectroscopy, Nuclear magnetic resonance

## 1. Introduction

The TGS crystal family, with the chemical formula (NH<sub>2</sub>CH<sub>2</sub>COOH)<sub>3</sub>·H<sub>2</sub>SO<sub>4</sub>, is one of the well-known ferroelectric materials useful for room temperature IR detector applications. Pyroelectric detectors based on TGS are uniformly sensitive to radiations in the wavelength range from ultraviolet to far-IR and do not require cooling as compared to quantum detectors, where low cooling is required. The crystal structure of TGS is monoclinic below  $T_c$  (49°C). There are two chemical formulas in the elementary cell of the lattice, and the crystal is monoclinic with the space group P2<sub>1</sub> in the ferroelectric phase. Above the  $T_c$ , in the paraelectric phase, there are two mirror planes at  $y = 0.25$  and  $0.75$ , and space group P2<sub>1/m</sub>. The ferroelectric effect is associated with the asymmetrical arrangement of the glycine group G I versus the mirror plane and the proton exchange between glycine groups G II and G III associated with the exchange role of zwitterions between two groups [1]. The b-cut/(010) crystals are used for detector fabrication, which is also a cleavage plane. Single crystals of TGS are usually grown from an aqueous solution by the method of temperature lowering or solution evaporation [2-7, 9-16]. TGS crystals weighing more than 100 g have also been grown from solution with ethyl alcohol addition [8].

To counter the drawbacks cited above while maintaining the same basic structure, many modifications to TGS have been proposed and evaluated for pyroelectric infrared (PIR) detection applications. These modifications include deuteration of TGS (DTGS). L-alanine has the effect of introducing an internal electric field to produce poled TGS crystals and stabilizing the spontaneous polarization. This is because the alanine molecules possess an extra methyl group that prevents them from rotating within the lattice. The dipole it possesses is thus fixed with respect to the crystal structure and does not disappear at the  $T_c$ . The L-alanine LATGS crystals can be thermally cycled through the  $T_c$ . They will retain their spontaneous polarization, thereby avoiding the poling process. There is an increase in figure of merit (FOM) depending upon the L-alanine content in the TGS lattice. The uniformity of L-alanine doping in the TGS lattice is also difficult to attain. It can be inferred that deuteration of TGS provides a marked improvement to the  $R_V$  and also increases the  $T_c$  to 60°C, depending on the deuteration level. This is extremely desirable as it increases the temperature range of detector operation. Bye and Keve [6] studied the pyroelectric properties of x-ray irradiated/field-treated TGS detectors and compared these with LATGS detectors. The improvements in FOMs of x-ray/field-treated TGS detectors were comparable to L-alanine-doped TGS detectors.

In the recent past, doped TGS crystals with organic molecules have been reported with encouraging results such as L-lysine, urea, urea + L-alanine, thiourea, guanidine, and others [11-16]. A higher performance and increase in range of the operational temperature were offered by TGFB

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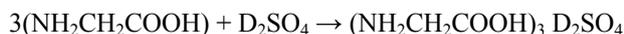
(Triglycine fluoberyllate) and DTGFB. However, the growth and processing of these crystals is dangerous due to the presence of toxic beryllium.

Deuterated Triglycine (DTGS) crystal has a Curie temperature, which can be raised to 57-62°C thus the temperature ranges of the devices made of it can also be raised. L-alanine doped deuterated triglycine sulfate (DTGS-LA) crystal creates an inherent bias field due to the doping, preventing the crystal from depolarization, and the pyroelectric property is greatly increased.

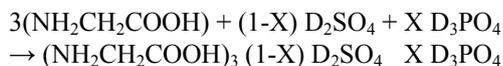
The pyroelectric figure of merit ( $FOM = p/\epsilon$ ;  $p$ -pyroelectric coefficient,  $\epsilon$ -dielectric constant) demands low permittivity and high pyroelectric coefficient. Substitution of glycine with alanine has improved the ferroelectric properties. The amino acids mixed TGS have low permittivity values compared with pure TGS. In the present investigation, deuterated phosphoric acid and the amino acid L-alanine have been substituted in order to improve the pyroelectric figure of merit of DTGSP. The amino acid alanine chosen has a similar structure to glycine. Studies on the advantages of DTGS and doped compounds over TGS as IR detectors have been reported. In the present work, pure and doped DTGS, and DTGSP with L-alanine are grown from solution. We have chosen this study to understand the incorporation of dopant and its bonding nature, with a view of obtaining an insight into the structural aspects.

## 2. Experimental Procedure

Deuterated triglycine sulfate (DTGS) was synthesized from the extra pure glycine (99.99%) deuterated sulfuric acid ( $D_2SO_4$ ) and deuterated water ( $D_2O$ ) as the solvent according to the reaction



Deuterated triglycine sulfo phosphate (DTGSP) was obtained by the chemical reaction of glycine, deuterated sulfuric acid, deuterated phosphoric acid, and deuterated water as the solvent with the following chemical composition:



where  $X = 0.2$ .

DTGSP doped with 2 grams of L alanine (DTGSP-LA) is also prepared in the present study.

Impurity concentration was minimized by successive recrystallization. The final solution was filtered using 0.1  $\mu m$  filter paper and kept in a beaker covered with perforated sheets to avoid contamination. After three days of evaporation, solution becomes supersaturated and small crystals were found to grow inside the beaker and are allowed to grow for a maximum possible dimension, and were carefully harvested and subjected to vibrational spectral characterization studies by Fourier transform infra red (FTIR)

and FT-Raman analysis, and is also analyzed by nuclear magnetic resonance studies.

FTIR spectral analysis in the range of 500-3500  $cm^{-1}$  was carried out by Thermo Nicolet FTIR spectrometer with a resolution of 8  $cm^{-1}$  using Globar (ETC Everglo) as the source of IR Radiation. FT-Raman spectra were recorded with a portable Horiba scientific Raman micro spectrometer in the range of 250-2500  $cm^{-1}$  using 785nm laser source. Nuclear magnetic resonance spectra of the grown samples were recorded with Anasazi Eft-60 NMR spectrometer in the  $^1H$ ,  $^{31}P$ , and  $^{13}C$  modes.

## 3. Results and Discussion

### 3.1. FT-IR Spectroscopic Analysis

Figure 1 depicts the FT-IR spectra of pure DTGS, DTGSP, and DTGSP-LA. In order to understand the existence of dopant and its bonding nature, with a view of obtaining an insight into the structural aspects of increased pyroelectric figure of merit, the present study has been undertaken. The observed wave numbers, relative intensities obtained from the recorded spectra, and the assignments proposed for the pure and doped DTGS crystal are given in table 1.

Degenerated modes of  $NH_3$  bending and  $C=O$ ,  $NH_4$ ,  $C-H$  and  $O-H$  stretching vibrations are observed. More bands were located at the same positions as those of pure TGS. Doped samples provide less resolution of bands. Some bands are broadened and some are narrowed. Degeneracy is more for doped samples than that for pure ones of DTGS. The internal modes of vibrations of the polyatomic group are known to occur in the 4000-500  $cm^{-1}$  range, while the lattice modes of vibrations due to the motion of one polyatomic group relative to another within the unit cell occur in the 500-10  $cm^{-1}$  range where most inorganic compounds absorb IR radiation.

The hydrogen bonding has a tendency to shift the stretching frequencies to a lower number. The vibrational peaks occurring at 1497  $cm^{-1}$  and 1603  $cm^{-1}$  are associated with the symmetric and antisymmetric vibrations of  $COO^-$  respectively, and indicate the presence of glycine as a zwitter ion. The strong sharp band at 1703  $cm^{-1}$  due to the stretching of  $C=O$  indicates the presence of the glycine molecule as  $NH_3^+CH_2COOH$  (glycinium ion) and strongly suggests the presence of both zwitter and glycinium ions. Normally, in the undoped DTGS crystals, the rear three glycine molecules per molecule of  $H_2SO_4$ , two exist as a glycinium ion and the third in a zwitter ion configuration. The existence of the glycine in the zwitterion configuration does not seem to be convincing for the case of  $H_3PO_4$ -doped TGS samples, because the hydrogen in  $H_3PO_4$  would prefer to be accepted by the  $COO^-$  of the zwitterions to form a glycinium ion rather than remain isolated in the crystal lattice [3]. Hence, all glycine molecules would rather exist as glycinium ions. In contrast, the presence of both the zwitter and glycinium ions in doped samples can be

understood only in terms of the very low incorporation of  $H_3PO_4$  into the crystal lattice as evidenced from the compositional analysis. Since no major shifts or additional peaks corresponding to the internal modes in the mid-IR region have been observed, the formation of any other complex compound in the doped DTGS crystals is ruled out.

In order to ascertain the presence of phosphorus as  $PO_4^{3-}$  or  $HPO_4^{2-}$ , doped samples were investigated in the infra-red region of the spectrum. An absorption peak around  $576\text{ cm}^{-1}$  was observed in all the samples attributing the  $SO_4^{2-}$  ion vibration. The peaks at  $563\text{ cm}^{-1}$  and  $542\text{ cm}^{-1}$  in the doped samples clearly confirm the presence of phosphorous [6] It is found that the IR spectra of doped TGS crystals closely resemble those of the undoped crystals with a slight shift suggesting that the crystal structures are similar with internal symmetry arrangements.

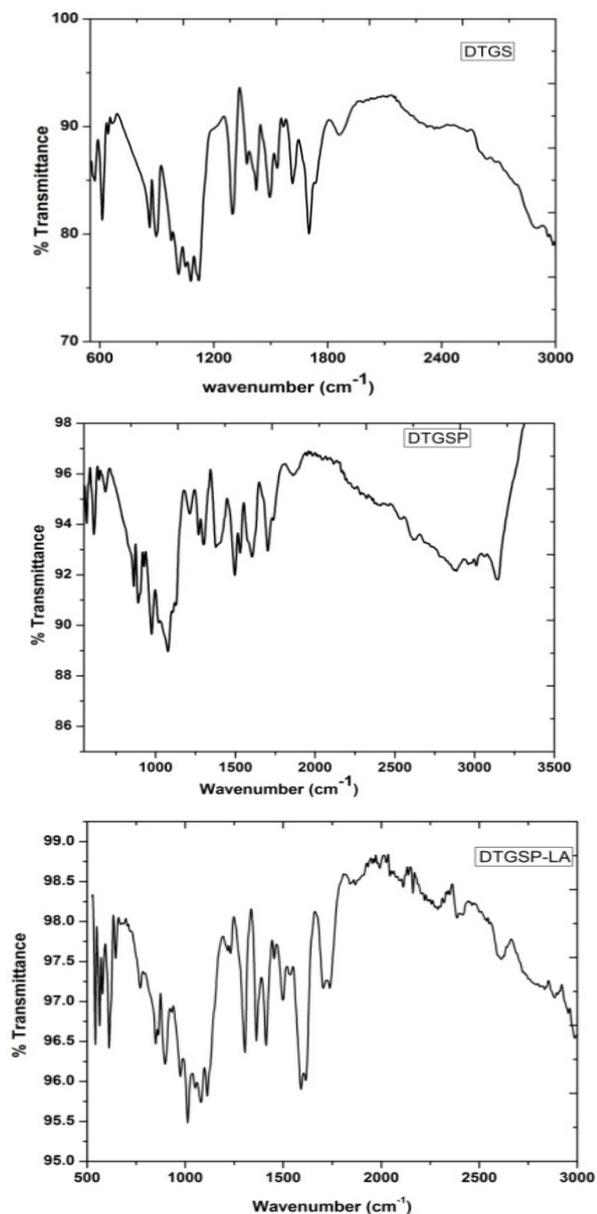


Figure 1. FTIR Vibrational spectra of pure and doped DTGS crystal

Table 1. Observed IR bands and their assignment for un-doped and doped DTGS

DTGS wave number ( $\text{cm}^{-1}$ )	DTGS(0.8)-P(0.2) wave number ( $\text{cm}^{-1}$ )	DTGS(0.8)-P(0.2)-LA wave number ( $\text{cm}^{-1}$ )	Assignment of vibration
		542w	$PO_4^{3-}$
	563m	563m	$PO_4^{3-}$
567w	-	-	$\nu\text{COO}^-$
576w, br	576	577w	$\nu\text{SO}_4^{2-}$
613s	611m	611m	$\delta\text{C-N}$
643vw	644vw	645w	$NH_3^+$
668m	-	667w,sh	$\text{COO}^-$ scissoring
-	684w	685w,sh	$\nu\text{S-H}$
862m	861m	864	$\delta\text{C-C}$ out of plane
897s	892s	896s	$\nu\text{NH}_3$
	927w	933w	$\nu\text{P-O-H}$
	974s	976s	$\nu\text{C-C-N}$
977vw	974s	976s	$\nu\text{C-C-N}$
1013w	1017vw	1011vw	$\omega\text{CH}_2, \delta\text{C-C}$
1050w		1050w	$\nu\text{C-N}$
1078w	1076s	1080s	$\nu\text{C=O}$
1121w	1108-1127m	1113m	$\rho\text{CH}_2, \nu\text{C-C}$
1299s	1300s	1305s	$\delta\text{CH}_2$ glycine
1375vw	1378m	1362w	$\delta\text{CH}_2$ glycine
-	-	1412	$\nu\text{S}\text{COO}^-$
1424m	-	-	$\nu\text{C-S}$
1495m	1497s	1500s	$\nu\text{NH}_3^+$
1535vw	1528w	-	$\delta\text{NH}_3^+$
1569vw	-	-	$\nu\text{as}\text{COO}^-$
	1603m		$\nu\text{as}\text{COO}^-$
1614w	-	1615w	$\nu\text{as}\text{COO}^-$
1702s	1703s	1703w	$\nu\text{C=O}$
1737vw	1739vw	1738w	Amide group
1862vw	1863w	1868w	Combinations
2017-2536vw	2008-2538vw	2026-2551 vw	Overtone

$\nu$ , stretching;  $\delta$ , deformation;  $\rho$ , rocking;  $\omega$ , wagging;  $\gamma$ , bending

### 3.2. FT-Raman Spectral Analysis

Raman spectra of the pure and doped DTGS crystals were recorded in the range from  $300\text{--}1800\text{ cm}^{-1}$  is shown in figure 2. By using the spectral data of  $SO_4$ ,  $PO_4$ ,  $CH_2$ ,  $NH_3$ ,  $C-H$ , and by comparing the spectra of the different samples, we have assigned the observed lines to the vibrations of the characteristic groups. The vibrational assignments are given in table 2. The low frequency vibrations are assigned to vibration and translation of glycine molecules relative to their linking bonds. The vibrations from  $319\text{--}400\text{ cm}^{-1}$  are assigned to the vibrations and translations of glycine molecule. The relative intensities of the glycine internal vibration remain almost unchanged, which confirms that doping with  $D_3PO_4$  and L-alanine does not alter the crystal structure with internal arrangements in the symmetries of groups in the unit cell.

According to Hoshino [20] one of the glycine groups exists as a zwitter ion while the other two glycine groups have protonated carboxyl groups, which have taken protons from the sulphuric acid.

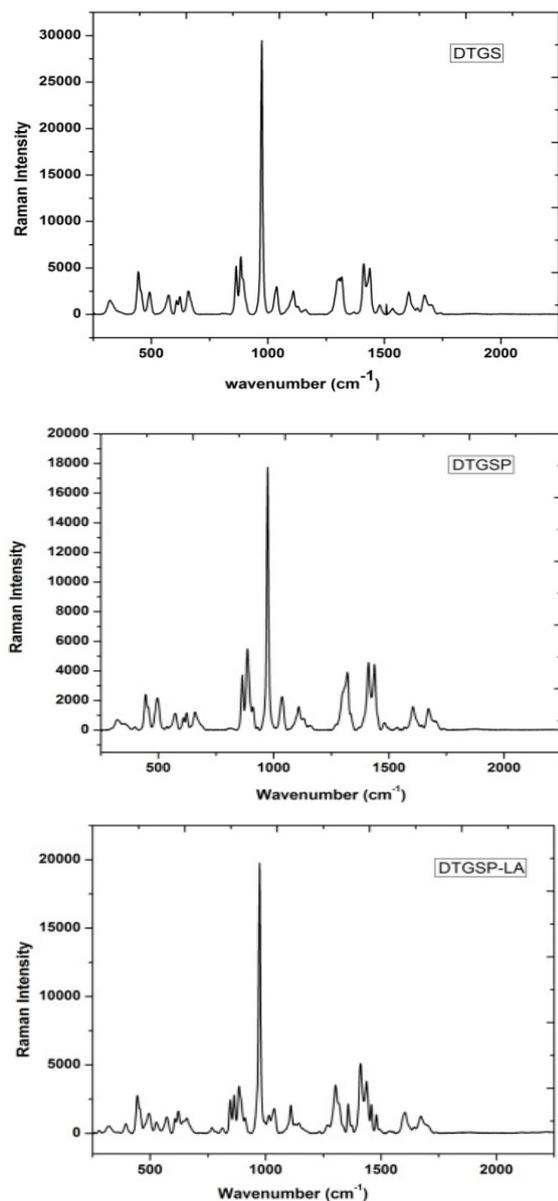


Figure 2. FT - Raman spectra of pure and doped DTGS crystal

The spontaneous polarization reversal in TGS is due to the proton transfer between glycine and glycinium ions. The switching mechanism can be confirmed by the existence of a dipolar ion in the unit cell of TGS. The bands at  $1359\text{ cm}^{-1}$  and  $1411\text{ cm}^{-1}$  indicate the presence of the zwitter ion in the DTGS crystal.

Considering the fact that  $\text{PO}_4^{3-}$  ions are replacing the  $\text{SO}_4^{2-}$  ions partially as evidenced by the vibrational spectra analysis, the extra proton provided by  $\text{D}_3\text{PO}_4$  molecule is expected to combine with the zwitter ion and hence, no transformation takes place between the glycinium ion and the zwitter ions wherever  $\text{PO}_4^{3-}$  ions are replacing  $\text{SO}_4^{2-}$  ions. The  $\text{NH}_3$  stretching modes appear as broad bands and therefore, could not be assigned and are not used for analyzing the effect of alanine doping. The bands at  $1110\text{ cm}^{-1}$  and  $1604\text{ cm}^{-1}$  are sensitive to doping. In the FT- Raman spectra of DTGS doped with  $\text{D}_3\text{PO}_4$  and  $\text{D}_3\text{PO}_4$  with alanine, some peaks were

shifted to a considerable range compared to pure DTGS. A change in the intensities of peaks was also observed. The amount of polarizability change will determine the Raman scattering intensity. So, we can infer that the change in the intensity of the peaks may be due to incorporation of dopants.

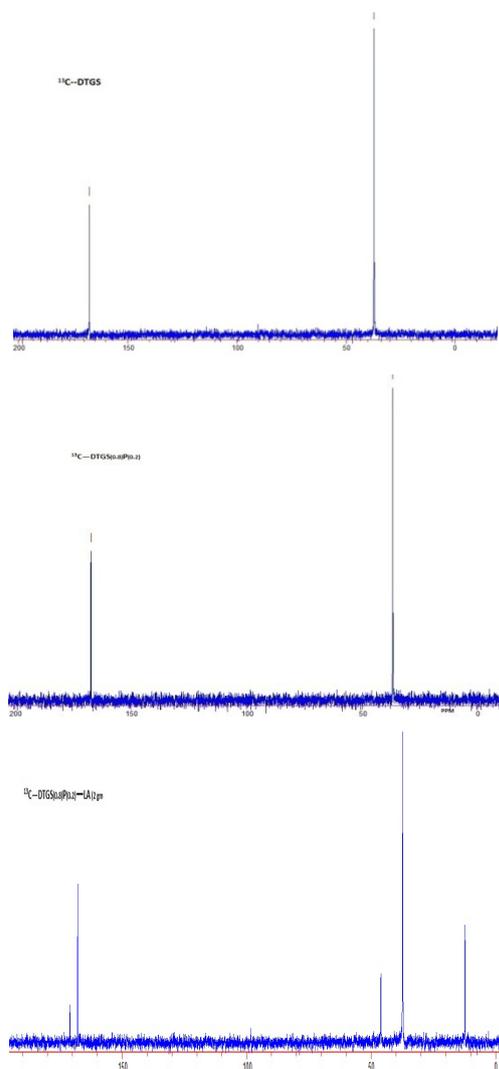
Table 2. Vibrational assignment for observed Raman spectra of pure and doped DTGS crystal

DTGS wave number ( $\text{cm}^{-1}$ )	DTGS(0.8)-P(0.2) wave number ( $\text{cm}^{-1}$ )	DTGS(0.8)-P(0.2)-LA wave number ( $\text{cm}^{-1}$ )	Assignment of vibration
322	319w	319w	$\delta^{\text{CCN}}$ (GI)
-	341	-	$\delta^{\text{CCN}}$ (GII)
-	400	393 w	$\delta^{\text{CCN}}$ (GIII)
445	443	445 m,sh	$\nu_2\text{SO}_4^{2-}$
492	496	496 m	C-CO bend
573	572	570 m	C-CO bend
608	609	609 w	$^{\text{O}}\text{COO}$
621	622	623 m	$\nu_4\text{SO}_4^{2-}$
659	658	658 sh	O-C-O bend ( GIII)
-	-	767 w	
-	-	813 w	
-	-	847 m	
862	863,886, 911	866 m	C-C stretch
884	(3 lines, W)	884	C-C stretch
973	973	975	$\nu_1\text{SO}_4^{2-}$
1037	1035	1038	$\nu^{\text{C-N}}$
1110	1110	1110	$\text{NH}_3$ rocking
1130	1131	-	$\text{NH}_3$ rocking
1163	1160	-	$\text{NH}_3$ rocking
-	-	1145	$\text{NH}_3$ rocking
-	-	1269	
1304	-	1304	$\text{CH}_2$ wagg/twist
1316	1320		$\text{CH}_2$ wagg/twist
		1359	$\text{CH}_2$ wagg/twist
1411	1413	1411	$\nu^{\text{C-O Sym}}$ (GI/GII)
1438	1438	1440	$\delta^{\text{CH}_2}$
1479	1480	1481	$\delta^{\text{CH}_2}$
1535	1538	-	$\delta^{\text{NH}_3}$ asymm
1604	1605	1603	$\delta^{\text{NH}_3}$ asymm
1672	1674	1676	$\nu^{\text{C=O}}$ (GI)
1703	-	-	Amide
	1738	1740	Amide

### 3.3. Nuclear Magnetic Resonance (NMR) Spectra Analysis

Carbon-13 NMR ( $^{13}\text{C}$  NMR) is the application of nuclear magnetic resonance spectroscopy to carbon. It is analogous to proton NMR and allows the identification of carbon atoms in an organic molecule just as the proton NMR identifies

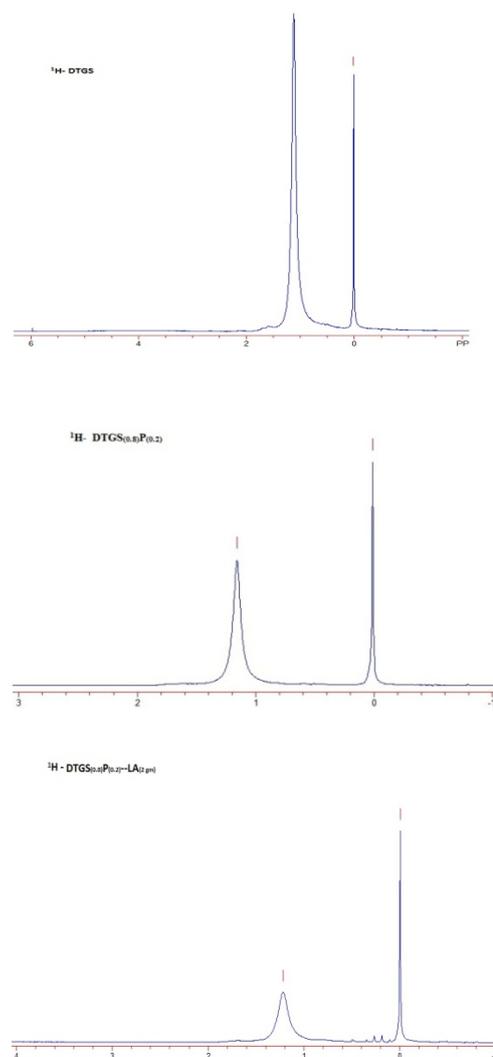
hydrogen atoms. The  $^{13}\text{C}$  NMR is directly above the carbon skeleton not just the proton to which it is attached. The number of signals tells the number of different carbons, and the splitting signal tells the number of hydrogen attachment, which depends on resolution and concentration due to the low isotopic abundance. In our study, samples are dissolved in deuterated water and  $^{13}\text{C}$  NMR spectra are recorded for DTGS, DTGSP and DTGSP-LA, and are shown in figure 3. The peak at 167 ppm found in all the three samples is due to  $\text{C}=\text{O}$ , and the one around 37 ppm found in all the three samples is due to  $\text{R}_3\text{-CH}$  bond, wherein the R groups won't necessarily be simple alkyl groups. The peak at 46 ppm confirms  $\text{C-NH}_2$  and  $\text{C-CH}_3$  forms a peak at 12 ppm in the sample, which validate our study.



**Figure 3.**  $^{13}\text{C}$  NMR spectra of undoped and doped deuterated triglycine sulphate

The application of nuclear magnetic resonance in NMR spectroscopy, with respect to hydrogen nuclei within the molecule of a substance, is used to determine the structure of its molecules, is proton ( $^1\text{H}$ ) NMR. The isotope of hydrogen, deuterium will not give any peak as its spin is zero. NMR spectra are recorded in solution with a small amount of 0.1%

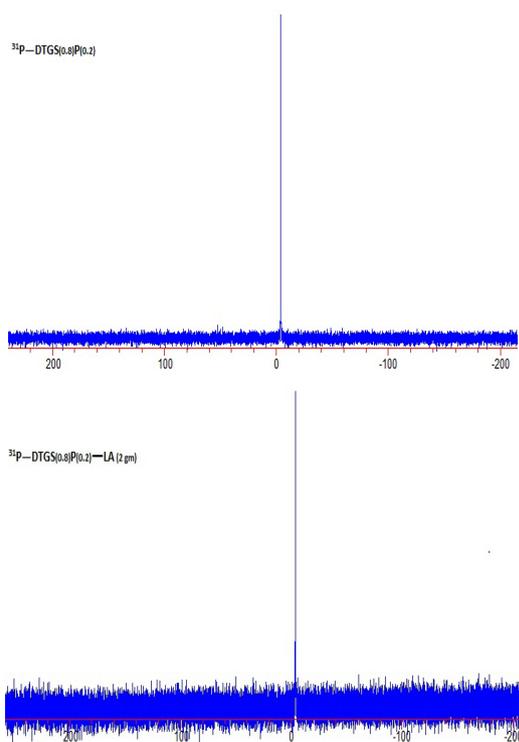
tetra methyl silane ( $\delta=0$  ppm) and solvent protons must not be allowed to interfere. Hydrogen nuclei are sensitive to the hybridization of the atom to which it is attached and to electronic effects. De-shielded nuclei resonate at higher  $\delta$  values whereas shielded nuclei at lower values. Electron withdrawing causes a down field shift of 1-4 ppm for H atoms on aliphatic C atom. The labile protons ( $-\text{OH}$ ,  $-\text{NH}_2$ ,  $-\text{SH}$ ) have no characteristic chemical shift. Such resonance can be identified by the disappearance of a peak when treated by  $\text{D}_2\text{O}$  as deuterium will replace a protium atom and is called  $\text{D}_2\text{O}$  shake. Acidic protons may be suppressed when a solvent containing acidic deuterium ions is used. In our study, we have used acidic  $\text{D}_3\text{PO}_4$ ,  $\text{D}_2\text{SO}_4$ , and  $\text{D}_2\text{O}$  for making DTGS and DTGS doped with deuterated phosphoric acid. The  $^1\text{H}$  NMR spectra of the samples recorded are shown in figure 4. The peak at 0 ppm corresponds to that of TMS and the one at 1.2 ppm to  $\text{CH}_2$ .



**Figure 4.**  $^1\text{H}$  NMR spectra of pure and dopant substituted DTGS

$^{31}\text{P}$  nuclear magnetic resonance is conceptually the same as proton ( $^1\text{H}$ ) NMR as both have a nuclear spin of  $\frac{1}{2}$ , which makes the spectra relatively easy to interpret.  $^{31}\text{P}$  NMR is an excellent technique for understanding the structure of

organic and metal coordination complexes containing phosphorous. While  $^1\text{H}$  NMR spectra use tetra methyl silane as the reference, the chemical shift in  $^{31}\text{P}$  is referenced with respect to 85% phosphoric acid ( $\delta=0$ ), which is used as an external standard due to its reactivity. Chemical shift in  $^{31}\text{P}$  NMR depends on the concentration of the sample, the solvent used, and the presence of other compounds. This is because the external standard does not take into account the bulk properties of the sample.  $^{31}\text{P}$  spectra are recorded with all proton signal decoupled  $^{31}\text{P}\{-^1\text{H}\}$ , giving rise to a single, sharp signal per unique  $^{31}\text{P}$  molecule, which depends on the electron environment of each phosphorous nucleus. The  $^{31}\text{P}$  NMR spectra recorded for the DTGSP and DTGSP-LA are shown in figure 5. The 85%  $\text{H}_3\text{PO}_4$  signal will appear as part of the sample NMR spectrum and thus be set to 0 ppm. In the recorded spectrum, peak appearance at -3.647 ppm at a downfield of -133.42 Hz is indicative of  $\text{O}=\text{P}(\text{OR})_3$  bond in the sample which again splits into -3.53ppm and -3.73ppm at the down field of -129.43 Hz and -136.6 Hz due to the change in the electronic environment due to the addition of 2 gms of L-alanine.



**Figure 5.**  $^{31}\text{P}$  NMR spectra of substituted and un-substituted deuterated triglycine sulphate

## 4. Conclusions

FTIR studies show that in all the spectra there is broadening of the band due to OH stretch of COOH and NH of  $-\text{NH}_3^+$ , and some of the bands are either narrowed or broadened in the spectra of the mixed crystals, which is a clear evidence of the presence of amino acid in the doped crystal. Based on the broadening of the peak in FTIR

spectrum, we confirm the co-existence of  $\text{PO}_4^{3-}$  and L-alanine in DTGS crystal, which does not change the crystal structure of symmetries of groups in the unit cell with a possibility of change in the bond length and bond angles, which in turn constitute a change in the pyroelectric figure of merit compared with TGS. FTIR and FT-Raman studies reveal that no major shift or additional peaks occur in their respective spectra, which rules out the possibility of formation of any other complex compound in alanine doped DTGSP crystal.

The spontaneous polarization reversal in TGS is due to the proton transfer between glycine and glycinium ions. This switching mechanism can be confirmed by the existence of a dipolar ion in the unit cell. Vibrational spectra of the samples under the present study indicate the presence of the zwitterions, which supports Hoshino's theory for the spontaneous polarization reversal. NMR spectroscopic analysis confirms the formation different functional group in the compound.

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