Raman Spectroscopic Studies on L-histidine, aniline Doped Triglycine Sulphate Single Crystals

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Abstract. Single crystals of triglycine sulphate (TGS) doped with L-histidine and aniline were studied by Raman Spectroscopy. The structure and symmetry of molecules, the nature of bonding and the effect of crystalline field on molecular vibrations were studied for pure and doped TGS. The characteristic group frequencies were identified and analysed for \( \text{H}_2\text{SO}_4 \) and glycine. The skeletal motion, lattice vibrational peaks were observed in the low wavenumber region. The site symmetry effect and the correlation field effect were studied from the splitting of vibrational bands. The observed Raman shift towards higher wave number region reveals that the symmetry reduction in doped TGS crystals. The broadening of Raman spectral line showed that a decrease in the hardness value for the doped crystals. Comparative studies of the Raman Spectra of pure TGS and doped TGS were also carried out.

1. Introduction

Triglycine sulphate [TGS] single crystal is one of the most extensively studied material as it possess excellent pyroelectric and ferroelectric properties. It exhibits strong absorption in most of the infrared region. This crystal is suitable to make speed broad band infrared pyroelectric detectors and vidicon. The crystal structure of TGS was reported by Hoshina et al [1]. The crystal is monoclinic in structure below and above the Curie temperature (49°C) [2]. Pure TGS crystals have some disadvantages over doped TGS crystals such as the ferroelectric domains possess high mobility at room temperature, easy depolarization by electrical and thermal means, microbial contamination with time during the growth and low Curie point. These disadvantages can be overcome by adding suitable impurities to the lattice sites of TGS crystals [3-5].

2. Materials and methods

Pure triglycine sulphate was synthesized [6] by taking glycine and sulphuric acid in the molar ratio 3:1. The required amount of sulphuric acid was diluted with double-distilled water. A calculated amount of glycine was added to the diluted sulphuric acid. The solution was heated until the salt became recrystallised. TGS aqueous solution was equilibrated with the amino acid L-histidine and aromatic compound aniline. FT Raman spectral measurements were carried out using Bruker IFS 66v FT-IR spectrometer attached with FRA 106 Raman module.

3. Results and discussion

In the present study, Raman spectra were recorded for pure TGS, L-histidine doped TGS and aniline doped TGS crystals and shown in Fig.3.1 – Fig.3.3. Raman vibrational modes for pure TGS and doped TGS crystals were identified and assigned.
3.1 Vibrational modes of glycine

In this section, the glycine group frequencies of NH$_3^+$, COO$^-$, CH$_2$, CH and C-C were assigned by using the reported Raman spectral data [7]. In the spectrum of pure TGS (Fig.3.1), CH$_2$ wagging/twisting is observed as a strong peak at 1302 cm$^{-1}$, but this mode is observed as a broad and strong peak for L-histidine doped TGS (Fig.3.2), and aniline doped with TGS (Fig.3.3) at 1302 cm$^{-1}$ and 1320 cm$^{-1}$ respectively. The observed splitting confirms the symmetry reduction in aniline doped TGS crystals. The Raman spectra show CH$_2$ rock mode as a strong band at 889 cm$^{-1}$ for all the three samples. The spectrum of pure TGS (Fig.3.1) shows a strong band corresponds to CH$_2$ bending at 1440 cm$^{-1}$. The spectrum of L-histidine doped TGS (Fig.3.2) and aniline doped TGS (Fig.3.3) show strong band corresponds to CH$_2$ bending at 1440 cm$^{-1}$ and 1439 cm$^{-1}$ respectively. The CH$_2$ scissoring is also observed as weak bands around 1482 cm$^{-1}$ for pure TGS and doped TGS crystals (Fig.3.1-Fig.3.3). The spectrum of pure TGS (Fig.3.1) shows a strong band at 2961 cm$^{-1}$ corresponds to CH$_2$ symmetric stretching vibrational mode but it is not observed for doped TGS. Another mode is also observed due to the CH$_2$ asymmetric stretching vibration at 2985 cm$^{-1}$ for pure TGS and L-histidine doped TGS as a strong band, but is observed as a very strong band at 2986 cm$^{-1}$ for aniline doped TGS. The CH$_2$ symmetric and asymmetric stretching modes are well resolved in pure TGS and L-histidine doped TGS as shown in (Fig.3.1 and Fig.3.2). In aniline doped TGS crystals, the CH$_2$ symmetric stretching mode is not resolved. In aniline doped TGS crystals, the CH$_3$ symmetric and asymmetric stretching modes also fall in the same region. The dopant (L-histidine or aniline) causes much broadening of the peaks in the spectra, compared to the pure TGS crystal. The line broadening effect is further confirmed by Aravazhi et.al [8]. This broadening leads to the unresolved CH$_3$ symmetric stretching and anti symmetric stretching modes in the region 2960-2990 cm$^{-1}$. The symmetry reduction also causes the broadening of spectral lines.

![Fig. 3.1. Raman Spectrum for pure TGS](image)

In the present study, the NH$_3^+$ stretching frequency is appeared as a medium broad band at 3008 cm$^{-1}$ (Fig.3.1) in pure TGS crystal. In L-histidine and aniline doped TGS crystals, (Fig.3.2 and Fig.3.3) show medium band at 3007 cm$^{-1}$ and 3018 cm$^{-1}$ respectively. The broadening of spectral line is due to the site symmetry and crystalline field effect in solids. In the pure TGS crystal (Fig.3.1) the asymmetric NH$_3^+$ deformation is observed at
1674 cm\(^{-1}\) as a medium broad band for L-histidine doped TGS and strong band for aniline doped TGS at 1675 cm\(^{-1}\) (Fig.3.2 and Fig.3.3). This reveals that the reduction in the crystal hardness as a result of dopant incorporation. The symmetric NH\(_3^+\) deformation mode is appeared as a weak band in doped TGS crystals. In pure and doped TGS crystals, the NH\(_3^+\) torsional mode/COO\(^-\)rock mode is appeared around 500 cm\(^{-1}\) as a medium band. The previous Raman studies on amino acids revealed that the COO\(^-\) asymmetric stretch is observed in the region 1605-1555cm\(^{-1}\), symmetric COO\(^-\) stretching is observed in the region 1425-1393 cm\(^{-1}\). In pure and doped TGS crystal (Fig.3.1-3.3), the COO\(^-\) symmetric stretching is observed as a strong band at 1414 cm\(^{-1}\) and COO\(^-\) asymmetric stretch is observed as a strong band at 1607 cm\(^{-1}\). For pure and doped TGS crystals, the COO\(^-\) scissoring and COO\(^-\) wagging modes are noticed as medium and weak band around 665 cm\(^{-1}\) and 579 cm\(^{-1}\) respectively.

Fig. 3.2. Raman Spectrum for L-histidine doped TGS crystals

3.2 Vibrational modes of H\(_2\)SO\(_4\)

The spectrum of pure TGS (Fig.3.1) shows the vibrational modes of H\(_2\)SO\(_4\) molecule. These modes also appeared in the spectra of L-histidine doped with TGS (Fig.3.2) and aniline doped with TGS (Fig.3.3). The vibrational modes of H\(_2\)SO\(_4\) have been assigned in all the three systems. All the three spectra show symmetric stretching mode (S[OH]\(_2\)), asymmetric stretching mode (S[OH]\(_2\)) and bending mode (SO\(_4\)). In pure TGS and doped TGS crystals, symmetric stretching mode, asymmetric stretching mode are appeared as a strong and very strong peak around 889 cm\(^{-1}\) and 978 cm\(^{-1}\) respectively.

Fig. 3.3. Raman Spectrum for aniline doped TGS crystals
The spectra of pure TGS (Fig.3.1), L-histidine doped TGS (Fig.3.2) and aniline doped TGS (Fig.3.3) show $\text{SO}_4^-$ bending modes as weak band around $613 \text{ cm}^{-1}$ and $629 \text{ cm}^{-1}$. The Raman spectra (Fig.3.1 and 3.2) show out-of-plane $\text{SO}_4$ stretching mode as a medium broad band around $1113 \text{ cm}^{-1}$ for pure TGS and L-histidine doped TGS. But it is observed as a strong broad band at $1114 \text{ cm}^{-1}$ for aniline doped TGS. In pure TGS and doped TGS crystals, the C-C stretching mode appeared as a strong band for pure TGS and L-histidine doped TGS, but it is observed as a medium band for aniline doped TGS at $1034 \text{ cm}^{-1}$.

The skeletal motions are observed as a weak bands around $331 \text{ cm}^{-1}$ and $462 \text{ cm}^{-1}$ in all the three systems. The Raman spectra (Fig.3.1-3.3) show the lattice vibrational modes in the region $100-250 \text{ cm}^{-1}$. The combination band is also appeared around $1482 \text{ cm}^{-1}$ as a weak band in pure TGS and doped TGS crystals. The combination band arises due to the $\text{S[OH]_2}$ asymmetric stretching mode and COO$^-$ rock /NH$_3^+$ torsion.

4. Conclusion

The Raman vibrational modes for pure TGS and doped TGS have been assigned and analysed. The correlation field effect and site symmetry reduction in solids have been discussed. A comparative study between pure and doped TGS crystals is also carried out. The line broadening was observed for doped TGS crystals compared with pure TGS. The spectral broadening reflected the crystal hardness as a result of dopant (L-histidine and aniline) incorporation. The broadening of the spectral lines in doped TGS crystals is due to the asymmetry of the L-histidine and aniline molecules, which are bigger in size than the glycine molecules and difficult to incorporate into the glycine site. The skeletal motion and lattice vibrational modes are also assigned.

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