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RESEARCH ARTICLE

OPTICAL, FTIR AND XRD ANALYSIS OF PURE AND L-HISTIDINE DOPED TRIGLYCINE SULPHATE CRYSTALS- A COMPARATIVE STUDY

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Abstract

Triglycine sulphate (TGS), an important ferroelectric material has been widely used in the fabrication of high sensitivity infrared detectors at room temperature. Single crystals of pure TGS and L-Histidine doped TGS crystals were grown by slow evaporation method at room temperature in this study. Both crystals were found to be highly transparent and full faced. The grown crystals were characterized by UV-Vis, FTIR and X-ray diffraction analysis. UV-VIS study shows that there is wide transparency in the visible region and the band gap energies were calculated. An FTIR spectrum was used to identify the presence of functional groups. The crystals grown belong to Monoclinic was inferred from the analysis of single crystal XRD.

Introduction

Ferroelectric crystals are interesting class of materials. They are similar to ferromagnetic materials in that, they exhibit hysteresis loops, spontaneous polarization and coercive field. Ferroelectric crystals have a number of practical applications and one of those is a pyroelectric infrared (PIR) detection. At the heart of every PIR detector is the pyroelectric crystal. The detectors use materials, such as triglycinesulphate (TGS) or lithium tantalite. Among ferroelectrics, triglycinesulphate (TGS) crystal is an interesting ferroelectric material which shows a typical second order ferroelectric phase transition at the Curie temperature of 49^0C [1-2]. It is a useful pyroelectric material in the fabrication of infrared detectors and pyroelectric vidicon tubes operating at room temperature [3-5]. Below the Tc, TGS possesses the polar point symmetry of group 2 of the monoclinic system, spontaneous polarization (Ps) arises along the b-axis and above Tc, it possesses the non-polar point group 2/m of the monoclinic system [6, 7]. It is observed by many researchers that undoped TGS crystals have some disadvantages over doped TGS crystals such as (i) the ferroelectric domains possess high mobility at room temperature, therefore it is necessary to stabilize domains, (ii) easy depolarization by electrical, mechanical and thermal means, (iii) microbial contamination with time during the growth and (iv) low Curie point etc. [4, 8-10]. In order to overcome these disadvantages, variety of dopants such as amino acids, organic and inorganic compounds have been introduced in TGS crystals to achieve effective internal bias to stabilize the domains and to obtain the desired pyroelectric and ferroelectric properties.
Amino acids are interesting materials for NLO applications as they contain a proton donor carboxyl acid (COOH) group and the proton acceptor amino (NH_2) group in them. Amino acids are widely utilized because they not only contain chiral carbon atoms directing the crystallization process in the noncentrosymmetric space group, but also possess zwitter ionic nature favouring crystal hardness [11].

Histidine (α-amino-β-imidazolepropionic acid) is characterized among the amino acids by the presence of the imidazole ring. It is the only standard amino acid having an imidazole side chain with pK_a near neutrality. In particular, Histidine is an interesting amino acid because it serves as a proton donor, proton acceptor and a

nucleophilic reagent. Histidine frequently occurs at the active sites of enzymes and also coordinates ions in larger protein structures [12]. It exists in orthorhombic and monoclinic forms [13]. Neutron and X-ray investigations on histidine hydrochloride have already been reported by Donohue et al [14]. L-Histidine salts can display high NLO properties due to the presence of imidazole group in addition to amino-carboxylate.

In the present paper, the effect of L-Histidine on the growth of TGS by slow evaporation method at room temperature has been studied. The grown crystals were characterized by UV-VIS, FTIR, powder XRD and single crystal XRD analysis. A comparative study on the results obtained for pure TGS and L- Histidine doped TGS crystal is detailed below.

2. Materials And Methods

Synthesis and crystal growth: Analar grade reagents Glycine and concentrated sulphuric acid (H_2SO_4) were dissolved in deionized water in the molar ratio of 3:1, and the solution was heated at 50^0C to obtain synthesized TGS salt. Glycine reacts with sulphuric acid as follows.

$3\ (NH_2CH_2COOH) + H_2SO_4 \rightarrow (NH_2CH_2COOH)_3.H_2SO_4$

The synthesized salt was again dissolved in double distilled water and then recrystallized by natural evaporation process. This process was repeated two times to improve the purity of the material.

In the case of L-Histidine doped TGS crystals, 1g of L- Histidine was added as dopant to the saturated solution of pure TGS. The seed crystals were obtained over a period of five days and were kept in the parent solution to get good quality crystals. Highly transparent and full faced crystals were obtained within two weeks on doping with L-Histidine. The photographs of the as grown crystals of pure and L- Histidine doped TGS crystals are shown in Figure 1(a) and Figure 1(b) respectively.

3. Results And Discussion

3.1 UV-Visible Analysis

Transmission spectrum is very important for any nonlinear optical (NLO) material, because a nonlinear optical material can be of practical use only if it has wide transparency window. The UV–Visible spectrum was recorded using SHIMADZU UV-Spectrometer 1601 in the range of 200 to 1000 nm. Optically polished crystal plates of 1.5 mm thickness were used for the measurement.

The transmittance graph for the pure and L-Histidine doped TGS crystals are shown in the Figure 2. The lower cut off region for pure TGS is obtained at 224 nm and band gap is found to be 5.54 eV. The cut off wavelength is 262 nm and band gap is found to be 4.74 eV for L-Histidine doped TGS crystal. Almost there is a steady transmittance in the visible region. From the UV-Visible spectrum, it is found that both pure and doped triglycinesulphate crystal is conveniently transparent from 380 to 1000 nm with around 80% of transmittance.

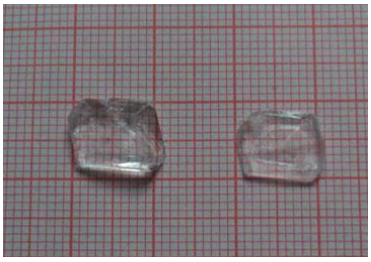

Figure 1(a). The photograph of the as grown crystals of pure TGS

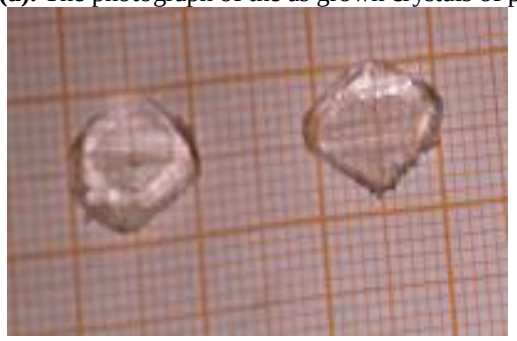

Figure 1(b). The photograph of the as grown crystals of L-Histidine doped TGS

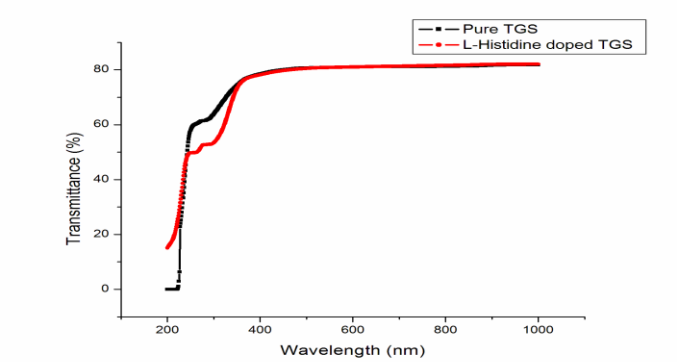

Figure 2. UV- Visible Transmission spectra of Pure and L-Histidine doped TGS crystals.

3.2 Fourier Transform Infrared Analysis

Fourier transform infrared (FTIR) was recorded in the range 400-4000cm^{-1} using the Perkin Elmer grating infrared spectrophotometer. The sample used was in pellet form mixed with KBr. The resulting spectrum for pure TGS and L-Histidine doped TGS are shown in the Figure 3 and Figure 4 respectively. FTIR spectral assignments of pure TGS and L-Histidine doped TGS crystal are given in Table 1.

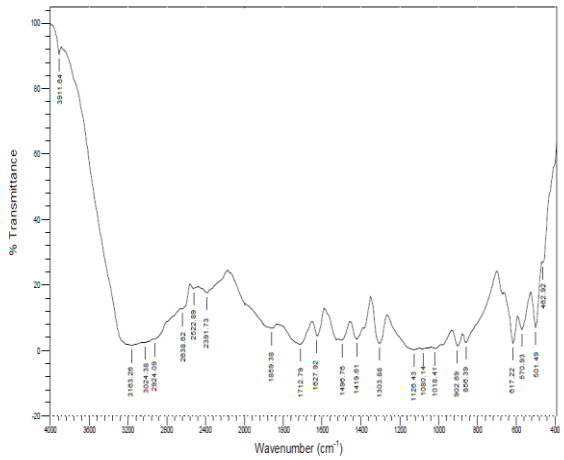

Figure 3. FTIR spectrum of pure TGS crystal.

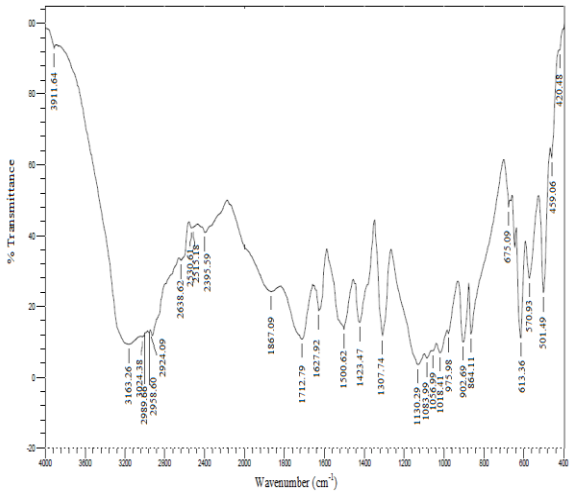

Figure 4. FTIR spectrum of L-Histidine doped TGS crystal.

Table 1. FTIR spectral assignments of pure and L-Histidine doped TGS crystals.

Wavenumber (cm^{-1})		Vibrational Band Assignments
Pure TGS	L-HistidineDoped TGS	
3163	3163	(NH_3^+) symmetric stretching / OH stretching
-	2989, 2958	CH_2 asymmetric Stretching
2924 2638 2522 2391	2924 2638 2530 2395	CH_2 stretching
1859	1867	(NH_3^+) asymmetric bending
1712	1712	Overtones and combinations
1627	1627	C=O stretching of COOH
1496	1500	(NH_3^+) asymmetric bending
1419	1423	NH_i bending+ NH_3 symmetric bending
1303	1307	asymmetric S=O stretching / CO_2 symmetric stretching+ CH_2 twisting
1126	1130	NC_2^{α} stretching + NC_3^{α} stretching
1080	1083	symmetric S=O stretching
-	1056	C-H in plane bending
1018	1018	SO_4 vibrations
902 856	902 864	C-C stretching
-	675	C-H out of plane bending
617	613	C_1/C_2 out of plane bending
570	570	NH_3^+ torsional oscillations
462	459	N-C-N stretching

3.3 Powder X-ray Diffraction

X-ray diffraction technique is a powerful tool to analyze the crystalline nature of the materials. Powder X-ray diffraction analysis was carried out by using PANalytical X-Ray diffractometer with CuKα radiation (λ=1.5406 Å for CuKα). The samples were scanned over the range 10º - 80º. The XRD pattern of grown pure and L-Histidine doped TGS crystals are shown in Figure 5 and Figure 6 respectively.

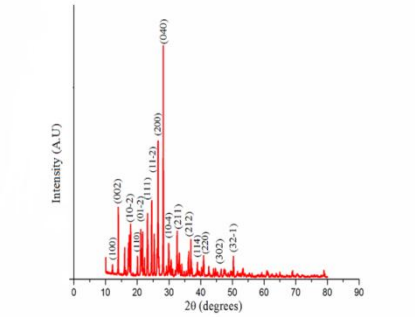

Figure 5. Powder XRD pattern of pure TGS crystal.

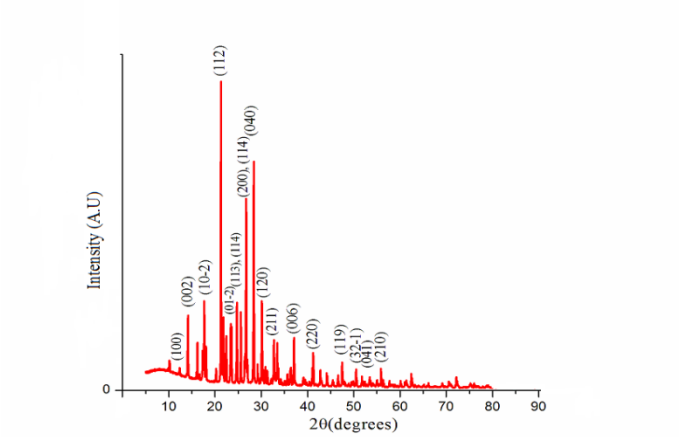

Figure 6. Powder XRD pattern of L-Histidine doped TGS crystal.

3.4 Single Crystal X-ray diffraction studies

The grown crystals of pure and doped TGS were subjected to single crystal XRD studies using ENRAF NONIUS CAD4-F single crystal X-ray diffractometer with MoKα (λ = 0.7107 Å) radiation. The lattice parameters and the cell volume of the pure and Histidine doped TGS crystals are presented in Table 2. It is observed from the X-ray diffraction data that both pure and doped TGS crystals belong to monoclinic system. The lattice parameters of pure TGS are in good agreement with the reported values in the literature [15]. In the case of doped TGS crystals, slight variation in the values of lattice parameter and cell volume is observed. The variations in the lattice parameters are due to the incorporation of L-Histidine molecule into the crystal lattice.

Table 2. Single crystal XRD data of pure and doped TGS crystals.

Lattice Parameters	Pure TGS	L-Histidine Doped TGS
a (Å)	5.830	5.727
b (Å)	12.234	12.639
c (Å)	9.419	9.147
α (°)	90	90
β (°)	104.64	105.57
γ (°)	90	90
Crystal System	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$
Volume ($Å^3$)	649.99	637.80

4. Conclusion

Optically good quality single crystals of pure TGS and L-Histidine doped TGS crystals have been grown by slow evaporation method. UV-Vis spectra showed that the grown crystal was optically transparent through 280-1000 nm and hence suggests the suitability of this material for optical devices. Powder X-ray diffraction analysis confirms the crystalline nature of grown crystal. The FTIR spectral analysis confirms the presence of functional groups in the crystals.

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