

Growth and Characterization of L-Alanine Doped TGS Crystal

P. R. Deepthi^{1*}, and J. Shanthi²

¹Department of Physics, The Oxford College of Engineering, Bangalore, Karnataka, India-560068

²Department Of Physics, Avinashilingam University for Women, Coimbatore, Tamilnadu, India- 641038

Abstract - 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 L-Alanine doped TGS was grown by slow evaporation method at room temperature in this study. The grown crystal was characterized by UV-Vis spectroscopy, FTIR spectroscopy, powder X-ray diffraction studies, and Vickers hardness analysis. L-Alanine doped TGS crystals were found to be highly transparent and full faced. The experimental results evidence the suitability of the grown crystal for optoelectronic applications

Keywords: Crystal growth; UV-Vis spectroscopy; FTIR spectroscopy; X-ray diffraction.

1. INTRODUCTION

Try Glycine Sulphate crystal is considered as one of the potential material for its wide range of applications namely, UV tunable laser, second harmonic generation, and pyro electric IR sensors due to its high pyro electric coefficient, optical transmission, and reasonably low dielectric constant [1-4]. It is a hydrogen bonded ferroelectric material having a typical second order phase transition at a Curie temperature of 49°C [5-7]. Below Curie temperature, ferroelectric and pyro electric materials are polar and possess a spontaneous polarization or electric dipole moment [8-11].

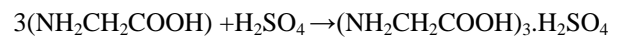
Despite its complicated chemical and crystallographic form, it is being studied for several years mainly for two reasons: firstly, its excellent pyro electric properties and high figure of merits make it suitable for use in the low-power detector applications where high directivities are required, e.g. in the setup of spectrometers. Secondly, it is one of the very few ferroelectrics known to exhibit a typical order-disorder type of phase transition, offering a spectrum of possibilities for understanding the basic mechanism of group-subgroup type of phase transitions in crystalline solids.

In Triglycine sulphate, glycine is one of the amino acids. The substitution of another amino acid – L Alanine in the place of glycine has been found to improve the crystal properties by way of contributing to effective internal bias in these crystals which, in turn inhibits ferroelectric switching giving permanently poled single domain crystal. This improved the device characteristics and hence Alanine mixed crystals of TGS family has been investigated by many researchers (Fang et al 1983).

In this paper the effect of doping TGS crystal with the amino acid L-Alanine and results obtained from various characterization studies have been reported. The doped crystal has been named as LATGS.

2. MATERIALS AND METHODS:

Synthesis and crystal growth: Analar grade reagents Glycine and concentrated sulphuric acid (H₂SO₄) were dissolved in deionized water in the molar ratio of 3:1, and the solution was heated at 50°C to obtain synthesized TGS salt. Glycine reacts with sulphuric acid as follows.



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.

To obtain doped TGS crystal, L-Alanine was added to the saturated mother solution. Highly transparent and full faced crystals were obtained within three weeks. The pure TGS and L-Alanine doped TGS crystals grown are colourless and are shown in figure

1 (a) and 1(b) respectively.

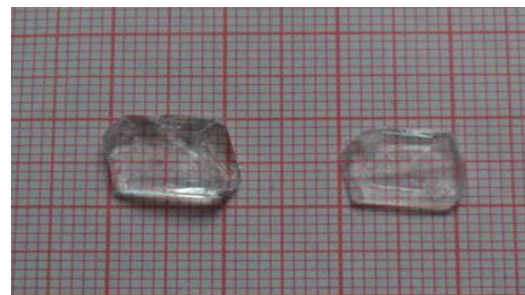


Fig 1(a). Photograph of pure TGS

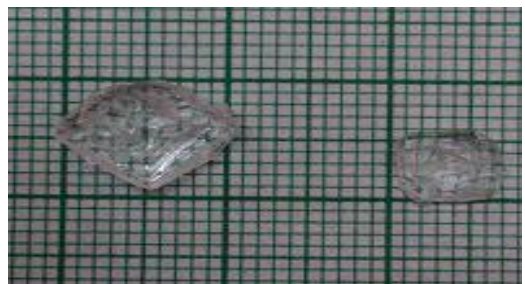


Fig 1(b). Photograph of L-Alanine doped TGS

TGS may be called glycine-di glyciniumsulphate with chemical formula (NH₃+CH₂COO⁻)(NH₃+CH₂COOH)₂SO₄²⁻). Of the three glycine groups contained in the asymmetric unit, two assume a completely planar configuration and the third one assumes a partially planar

configuration. The bond between two planar groups II and III are responsible for ferroelectric transition. Above the Curie temperature, glycine I molecule is split. Reversal of the polarization in the material is largely associated with the rotation of the glycine I group about the crystallographic 'a' axis to change into its mirror image [12].

3 RESULTS AND DISCUSSION:

3.1 UV-Vis spectral analysis

Optical properties of crystalline materials give information regarding the composition, nature and quality of the crystal. The optical transmission spectra of the grown crystal were carried out in the range of 200nm to 800nm covering the entire near-ultraviolet, visible, and near infrared region using SHIMADZU UV-160 Spectrometer to find the transmission range about the suitability of the grown crystal for optical applications. An optically polished single crystal was used for this study. The UV-Vis -NIR spectrum of the pure and doped TGS crystal is shown in fig 2 (a) and 2 (b) respectively. The UV cut off for the doped crystal was found to be 218 nm and the low absorption through the entire visible region is one of the most desired properties for the fabrication of optoelectronic devices. The band gap was calculated using the formula $E_g = \frac{hc}{\lambda}$ and the optical band gap is found to be 5.69 eV.

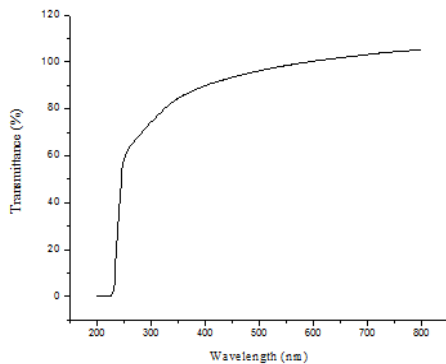


Fig 2 (a) . Optical Transmission spectra of pure TGS

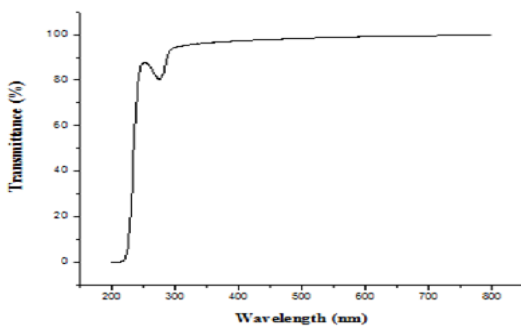


Fig 2 (b) . Optical Transmission spectra of L-Alanine doped TGS

3.2. Powder x-ray diffraction

X-ray diffraction technique is a powerful tool to analyze the crystalline nature of the materials. If the material to be investigated is crystalline, well defined peaks will be observed. Powder X-ray diffraction analysis was carried out by using PANalytical X-Ray diffractometer with Cu K α radiation. The sample was scanned over the range 20° - 70°. The XRD pattern obtained for the pure TGS and LATGS is shown in fig 3 (a) and 3(b) respectively.

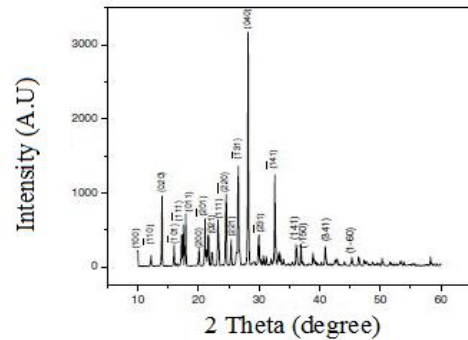


Fig 3 (a). Powder XRD pattern of pure TGS

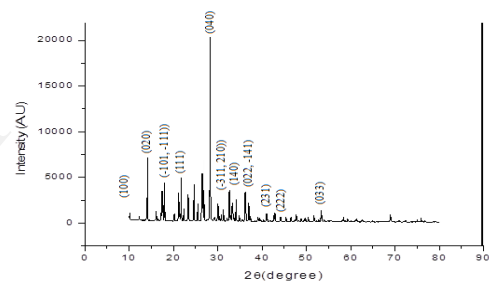


Fig 3 (a). Powder XRD pattern of L-Alanine doped TGS

3.3 FTIR spectral study

The Infrared spectral analysis is effectively used to understand the chemical bonding and it provides information about the functional group present in the synthesized compound. The FTIR spectra have been recorded in the range 400 to 4000 cm⁻¹. The FTIR spectra of pure TGS and L-Alanine doped TGS is shown in Figure 4(a) and 4 (b) respectively. The observed frequencies and their assignments for L-Alanine doped TGS crystal are listed in Table 1.

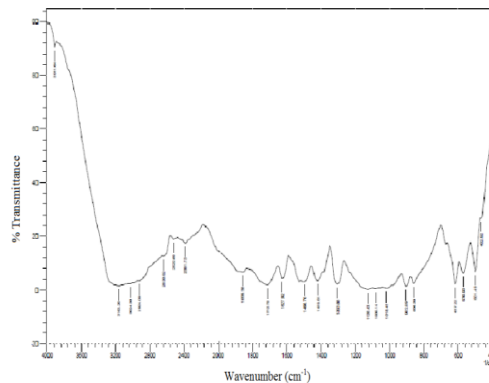


Fig 4 (a) FTIR spectrum of pure TGS

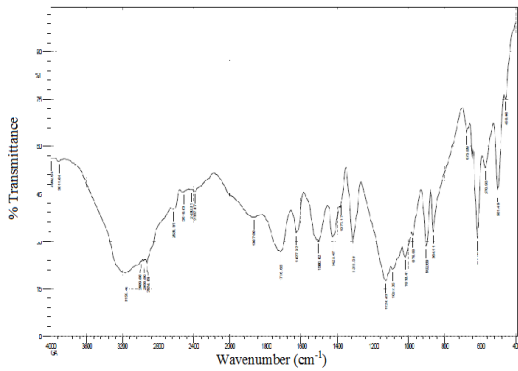


Fig 4 (b) FTIR spectrum of L-Alanine doped TGS

Table1. Frequencies and their assignments for L-Alanine doped TGS crystal.

| Wavenumber | Assignments |
|------------|--|
| 3159 | (NH ₃ ⁺) symmetric stretching |
| 2924 | CH ₂ stretching |
| 2630 | CH ₂ stretching |
| 1716 | Overtone and combinations |
| 1627 | Amide |
| 1500 | (NH ₃ ⁺) anti symmetric bending |
| 1423 | NH _i bending+ NH ₃ symmetric bending |
| 1311 | CO ₂ symmetric stretching+ CH ₂ twisting |
| 1126 | NC ₂ ^α stretching + NC ₃ ^α stretching |
| 902 | C-C stretching |
| 613 | C ₂ out of plane bending + C ₂ N torsion +C ₁ O out of plane bending |
| 501 | NH ₃ oscillation |

3.4 Vicker's Micro hardness Studies.

The hardness of a material is related to its bond strength and crystallographic orientation. The important property of any device material is its mechanical strength, represented by its hardness. Vicker's micro hardness indentations were made at room temperature with the load ranging from 10 g to 100 g. The indentation time was kept as 6 sec for all the loads. Vicker's micro hardness number, Hv, was calculated using the following equation:

$$Hv = 1.8544P / d^2$$

Where P is the applied load in Kg, d is the diagonal length of indentation impression in millimeter, and 1.8544 is a constant of a geometrical factor for the diamond pyramid.

The variation of load versus Vicker's hardness number is shown in Fig 5.

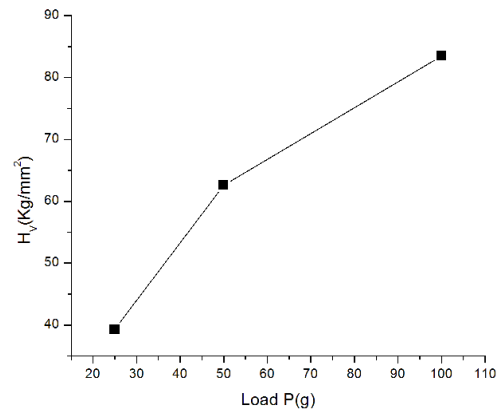


Fig. 5. The variation of Vicker's hardness versus load for L-Alanine doped TGS crystal.

Meyer's index number was calculated from Meyer's Law [13]. Meyer's index number was found to be 3 which suggest that L-Alanine doped TGS crystal belongs to soft material category [14]. The stiffness constant is calculated using the formula

$$C_{11} = (Hv)^{7/4}$$

The variation of load versus stiffness constant for L-Alanine doped TGS crystal is shown in Fig 6.

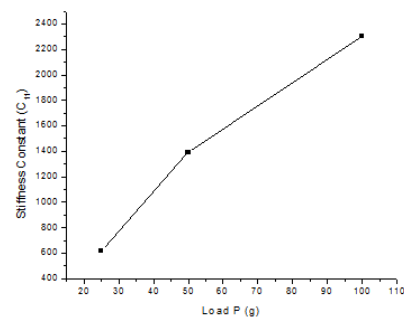


Fig. 6. The variation of stiffness Constant versus load for L-Alanine doped TGS crystal.

4. Conclusion.

Optically good quality single crystals of pure TGS and L-Alanine doped TGS crystals have been grown by slow evaporation method. UV-Vis spectra showed that the grown crystal was optically transparent through 200-800 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. Vicker's micro hardness test shows that the grown crystals belong to the category of soft materials.

REFERENCE.

- [1]. R.B.Lal and A.K.Batra, (1993), "Growth and properties of triglycinesulphate(TGS) crystals: review", *Ferroelectrics*, 142, pp.51-82.
- [2].H.P.Berman, "Improvement in the pyroelectric infrared radiation detector", 2, pp.123-128.
- [3]. S.Kielich,(1973), "Nonlinear optical and electro-optical properties of dielectrics and ferroelectrics", *Ferroelectrics*, 4, pp.257-282.
- [4]. G.Dolino,J.Lajzeroicz, and M.Vallade,(1970) " Second harmonic light scattering by domains in ferroelectric triglycinesulphate", *Physical Review B*, 2 , pp.2194-2200.
- [5]. M.E.Lines and A.M.Glass, (1977), *Principles and application of Ferroelectric and related materials*, Oxford University Press,Oxford, UK.
- [6]. Landolt-Bornstein, (1969), *Crystal and solid statePhysics*,Newseries,GroupIII,3,Springer,Newyork,NY,USA,.
- [7].S.Hoshino,Y.Okaya,andR.Pepinsky,(2008)" Crystal structure of the ferroelectric phase of (glycine)₃.H₂SO₄",*Physical Review*, 115, pp.118-121.
- [8].M.Banan, R.B.Lal and A.K.Batra, (1992), *J. Mater. Sci.*, 27, pp 2291.
- [9]. K. Meera, R. Muralidharan, P. Santhanaraghavan, R.Gopalakrishnan and P. Ramasamy, (2001), *J. Cryst. Growth*, 226, pp 303.
- [10]. G. Arunmozhi, S. Lancers-Mendez and E. de Matos Gomes, (2002), *Mater. Lett.*, 54, pp 329.
- [11]. A. J. JeyaprakashManoharan, N. Joseph John, V. Revathi, K.V. Rajendran and P.M.Andavan, (2011), *Indian J.Sci.Technol.*, 4, pp 688.
- [12].R W Whatmore, (1986), *Pyroelectric devices and materials*, *Rep. Prog. Phys.* 49, pp 1335.
- [13]. K.Jagannathan, S. Kalainathan and T Gnanasekaran, (2007) *Mater. Lett.* 61, pp 4485.
- [14]. Hanneman M (1941) *Metall. Manchu*, 23, pp 135.

IJERT