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RESEARCH ARTICLE

GROWTH AND STUDIES ON FERROELECTRIC MATERIAL L-PROLINE DOPED TGS SINGLE CRYSTALS FOR IR DETECTORS

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ABSTRACT

Single crystals of triglycine sulphate (TGS) doped with L-proline have been grown from aqueous solutions by low-temperature solution growth method. The Fourier Transform Infrared spectroscopy has been recorded in the range 400 to 4000 cm–1 and the functional groups of the grown crystals have been identified. The structural studies on the grown crystals were carried out by X-ray diffraction analysis technique and found that the grown crystal crystallizes in monoclinic structure. The lattice cell parameters of pure Triglycine sulfate are a = 9.5020 Å, b = 12.6010 Å, c = 5.271 Å. Ultraviolet-Visible spectra show that the grown crystals have wide optical transparency in the entire visible region. It is found that solubility of the samples increase with the increase in temperature. Density of the grown samples were determined by floatation. Since the work hardening coefficient is found to be more than 1.6, all the grown crystals of this work are in the category of soft materials. Thermal studies were also carried out.

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INTRODUCTION

Amino acid family of crystals over the years been subjected to extensive investigation by several researchers for their non linear optical properties (Jayaprakash Manoharan *et al*., 2011a, 2011b). The crystal of many inorganic derivatives of amino acids provides excellent crystals such as triglycine sulphate, L-arginine phosphate accepted for the fabrication of devices (Lineo 1977) Triglycine sulphate (TGS) is well known ferro electric material and it is widely used in fabricating thermal detectors, vidicons and image systems due to its second-order phase transition at room temperature and higher pyroelectric co-efficients as well (Beerman 1968; Putley 1970). The major drawback in TGS crystal is depolarization of the device performance. To overcome this, organic and inorganic dopants have been tried. The organic and inorganic dopants in TGS have solved the problem of depolarization. In L-alanine added TGS, the presence of extra methyl group in the place of a hydrogen atom resulted in stabilization of the structure (Fang 1983; Bye *et al*., 1972; Bhalla *et al*., 1983). The added advantage of doping results in reduced dielectric permittivity and hence the pyroelectic figure of merit was higher that's the undoped TGS (Ravi *et al*., 1995; Arunmozhi *et al*., 1997). Even though doping enhances the characteristics of TGS, it could not alleviate the proliferation of microbes.

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Since glycine and co-substituted amino acids are rich in nutrient and hence reducing their shelf life. In order to overcome this microbial problem, the partial substitution of phosphate in TGS was tried and it gives rise to enhanced characteristic and shelf life time of the solution. The practical substitution of an optically active molecule in the place of glycine d molecule causes an internal bias field, which makes the crystal permanently polarized (Nakatani 1973). Many authors investigated the effect of doping of various amino acids on TGS (Bye 1972; Aravazhi 1997a; 1997b; Meera *et al*., 2001). The effect of organic dopants on TGS and rare earth ions dopant with TGS have also been investigated (Meera *et al*., 2001; Mihaylova *et al*., 1996; Muralidharan *et al*., 2002; Selvarajan 2008). In recent years, the interest in studying the pure and doped TGS crystals has increased because of their promise in various devices. In the present work we have chosen the amino acid L-prolin as dopant because proline ions are expected to play a partial role for the spontaneous polarization in TGS crystal thereby increase the dielectric constant and Tc due to its intrinsic dipole moment. The objective of the present work was to investigate the effect of dlL-prolin addition on the growth and properties of TGS crystal.

Experimental

Synthesis of TGS

Triglycine sulphate (TGS) was synthesized (Jayaprakash *et al*., 2011a and Theresita shanthi *et al*., 2009), by taking glycine

and sulphuric acid in the molar ratio 3:1. Glycine reacts with sulphuric acid as follows:

$3(NH_2CH_2COOH)+H_2SO_4 \rightarrow (NH_2CH_2COOH)_3H_2SO_4$

The required amount of sulphuric acid was diluted with doubly distilled water. Then, the calculated amount of glycine was added and dissolved in diluted H_2SO_4. The solution was heated until the salt got recrystallized. Extreme care was taken during recrystallization to avoid the oxidation of glycine. Hence, the solution temperature was always maintained below 60°C. The recrystallized TGS salt was dissolved in doubly distilled water. In this way the natural impurity content of TGS salt was minimized. The doped samples were prepared by mixing 5 mol % of L-proline with TGS. Impurity contents in TGS were minimized by successive recrystallization process.

An important step to obtain good quality crystals is the use of high purity chemicals and hence analytical reagent (AR) grade of sulphuric acid, glycine and L-proline were used. The technique followed for the growth of L-proline doped TGS single crystals was solution method with slow evaporation technique. In accordance with the solubility data, the saturated solution of L-proline doped TGS was prepared in water at room temperature and maintained with continuous stirring by using a magnetic stirrer for about two hours to ensure homogeneous concentration over the entire volume of the solution. The homogeneous saturated solution was kept in glass vessels covered with perforated filter paper for slow evaporation. Repeated recrystallization was carried out to obtain good quality and transparent crystals. Seed crystal technique was also used to harvest large-size crystals. A photograph of the harvested L-proline doped TGS crystal is displayed in Figure 1. The growth period was 25-30 days.

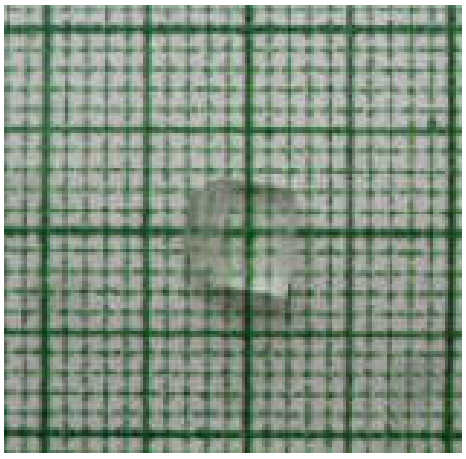

Figure 1. Photograph of grown L-proline doped TGS crystal

Characterization

As the growth of the crystal depends on the stability and growth temperature, the solubility of L-proline added TGS were found out. Solubility of grown crystal was determined in the temperature range between 30 and 50°C. Density of the grown crystal was determined by floatation method. Microhardness study of the grown crystals was carried out using Leitz Weitzler hardness tester fitted with a diamond indenter. A Varian Cary 5E UV-Visible-NIR spectrophotometer was used for optical transmission studies in the range 190-1100 nm. Single crystal XRD data for the grown single crystals were collected using an ENRAF NONIUS CAD4 diffractometer with MoK radiation (_=0.71073 Å). Powder X-ray diffraction pattern of the sample was obtained using a powder X-ray diffractometer (PANalytical Model, Nickel filtered Cu K radiations (_= 1.54056 Å) at 35 KV, 10 mA). To analyze the presence of functional group in pure and proline added TGS crystals, the FTIR spectrum was recorded in the range 4000 – 450 cm^{-1} using a Perkin-Elmer grating infrared spectrometer.The thermogravimetric and differential thermal analyses (TG/DTA) of the sample were carried out simultaneously using a Perkin Elmer thermal analyzer in nitrogen atmosphere at a heating rate of 10°C/minute for a temperature range of 35 -1000°C.

RESULTS AND DISCUSSION

Solubility

The temperature of the solution was maintained at a constant temperature and continuously stirred using a motorized magnetic stirrer to ensure homogeneous temperature and concentration throughout the entire volume of the solution. The saturated solution was allowed to reach equilibrium at a chosen temperature and then the solubility was analyzed gravimetrically (Selvarajan *et al* 2011, Sivakala 2014, 2016). A sample of the clear supersaturated solution was taken in a warm pipette and weighed. The solubility was estimated by evaporating about 25 ml of the solution in an oven at constant temperature. The same process was repeated for different temperatures and the solubility curve has been obtained and shown in figure 2. It is observed from the figure that the solubility of the sample increases with temperature, showing a positive solubility–temperature gradient in water. To choose a suitable solvent for single crystal growth from a solution, the solubility provides valuable information. Solubility corresponds to saturation and the growth rate of a crystal depends on its solubility and temperature. Solubility data provides the amount of material available for crystal growth at a particular temperature.

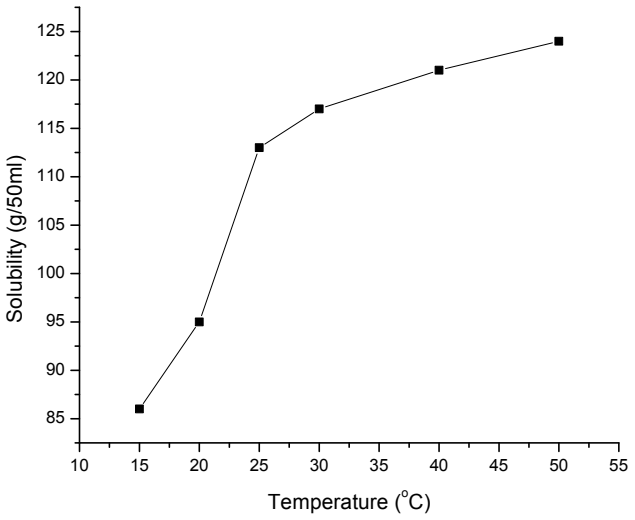

Figure 2. Solubility curve for L-proline added TGS crystal

Density

The floatation method was employed for the precise determination of density. Carbon tetrachloride of density 1.594 g/cc and bromoform of density 2.890 g/cc were used for this purpose. 10 ml of carbon tetrachloride was taken in a specific

gravity bottle and a small piece of the grown crystal was dropped into it. The crystal was at rest in the bottom of the bottle, then bromoform was gradually added until the crystal was in the suspended state. Now the density of crystal is equal to the density of solution. The density was calculated using the relation _=(w3-w1)/(w2-w1) where w1 is the weight of empty specific gravity bottle, w2 is the weight of the specific gravity bottle with full of water and w3 is the weight of the specific gravity bottle with full of the mixture of bromoform and carbon tetrachloride (Joseph John *et al* 2007, 2008). The density of L-prolin added TGS crystal determined by the floatation method is is found to be 1.702 which is well matched with the reported value.

Microhardness

Microhardness measurements were made using a diamond pyramid indentor on (010) plane of sample crystals. The distance between any two indentations was maintained to be greater than five times that of the diagonal length in order to avoid any mutual influence of the indentations. The loads ranging from 10 to 50 g were used for making indentations, keeping the time of indentation constant at 10s. From the results it is observed that as the load increases, the hardness is found to increase. This increase in hardness number can be attributed to the work hardening of the surface layers of the crystal. If the load is increased beyond 50 g crystals are observed to be ruptured. Figure 3 shows the variation of hardness number with load for the pure and L-proline added TGS crystals.

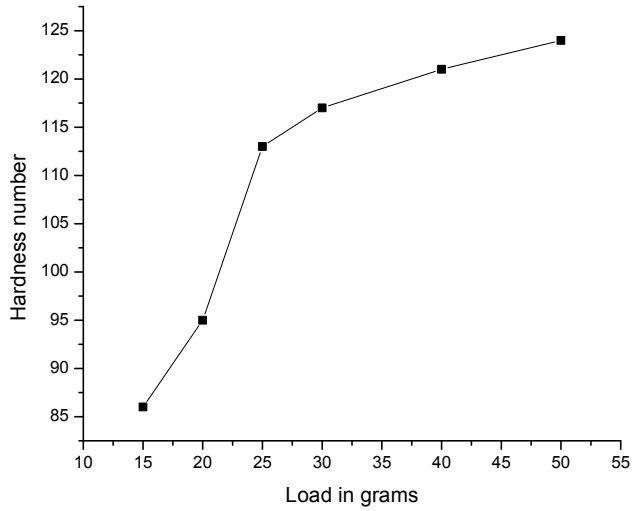

Figure 3. Variation of hardness number with load for the L-proline doped TGS crystal

UV-Visible-NIR Spectrum

The UV–Visible-NIR transmittance spectrum of pure and L-proline doped TGS crystals were recorded using an UV–Visible-NIR spectrophotometer at STIC, Cochin. The transparent behaviour of TGS in the entire UV-Visible-NIR region is clearly illustrated by its UV-Visible-NIR spectrum shown in Figure 4. It is also supported by the transmittance spectrum showing 100% transmittance in the entire UV-Visible-NIR region.

Structural Properties

The single crystal X-ray diffraction study was performed with a specimen cut from the grown pure and L-proline added TGS crystals. An Enraf-Nonius CAD4 diffractometer with MoK_α (λ = 0.71073 Å) radiation was used to obtain the cell parameters.

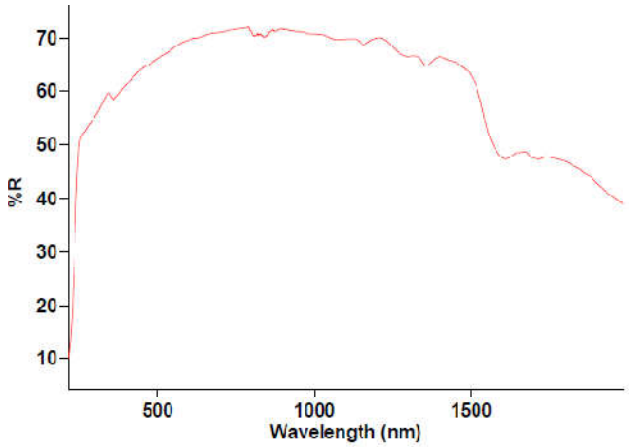

Figure 4. UV-visible NIR transmittance spectrum of L-proline doped TGS crystal

Computerized auto indexing was performed with an algorithm operating on difference vectors derived from the input reflections. The powder XRD pattern of L-PROLINE doped TGS single crystal is provided in Figure 5. The lattice parameters in table 1. The lattice parameters obtained in the present study compare well with that available in the literature.

Table 1. Lattice parameters of pure and L-proline doped TGS crystals

Slno.	parameters	value
1	a(Å)	9.502(3)
2	b(Å)	12.601(2)
3	c(Å)	5.271(3)
4	β(°)	105.82(2)
5	V(A^3)	650.53(1)

FTIR Spectrum

To analyze the presence of functional group in pure and proline added TGS crystals, the FTIR spectrum was recorded in the range 4000 – 450 cm^{-1} using a Perkin-Elmer grating infrared spectrometer. The sample used was in the pellet form in the KBr phase. Figure 6 shows the FTIR spectrum of L-proline added TGS crystals and the frequency of the observed bands and their assignments are listed in Table 2. Although it provides similar features as that of pure TGS spectrum, there is some variation in the absorption intensity of the peaks and the position of peaks, suggesting a wide range of interactions for the groups.

The broadening of the bands for doped TGS crystals clearly indicates the presence of L-proline. The FTIR spectra of L-proline added TGS crystal shows the higher energy region involving OH and NH stretching modes are less resolved than pure TGS. Similarly the SO_4 stretching modes in the lower energy region around 1133.32 cm^{-1} are also less resolved. These points to enhanced association of these groupings with the neighboring groups in the doped crystal. Hence it is presumed that in the crystal, the proline molecules would be brought very close to NH_3^+ and COOH groups of TGS through its alcoholic OH groups. The NH_3^+ group of proline can very well be placed near SO_4^{2-}.

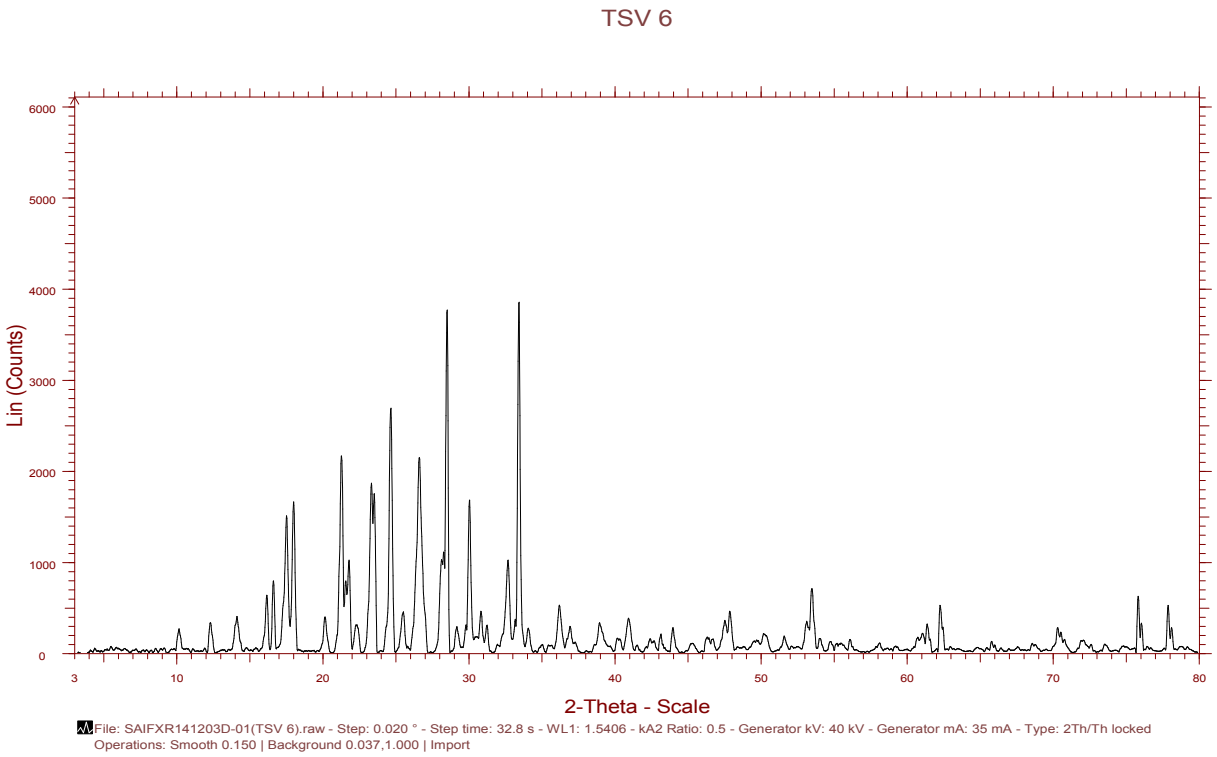

Figure 5. XRD pattern of L-proline doped TGS crystal

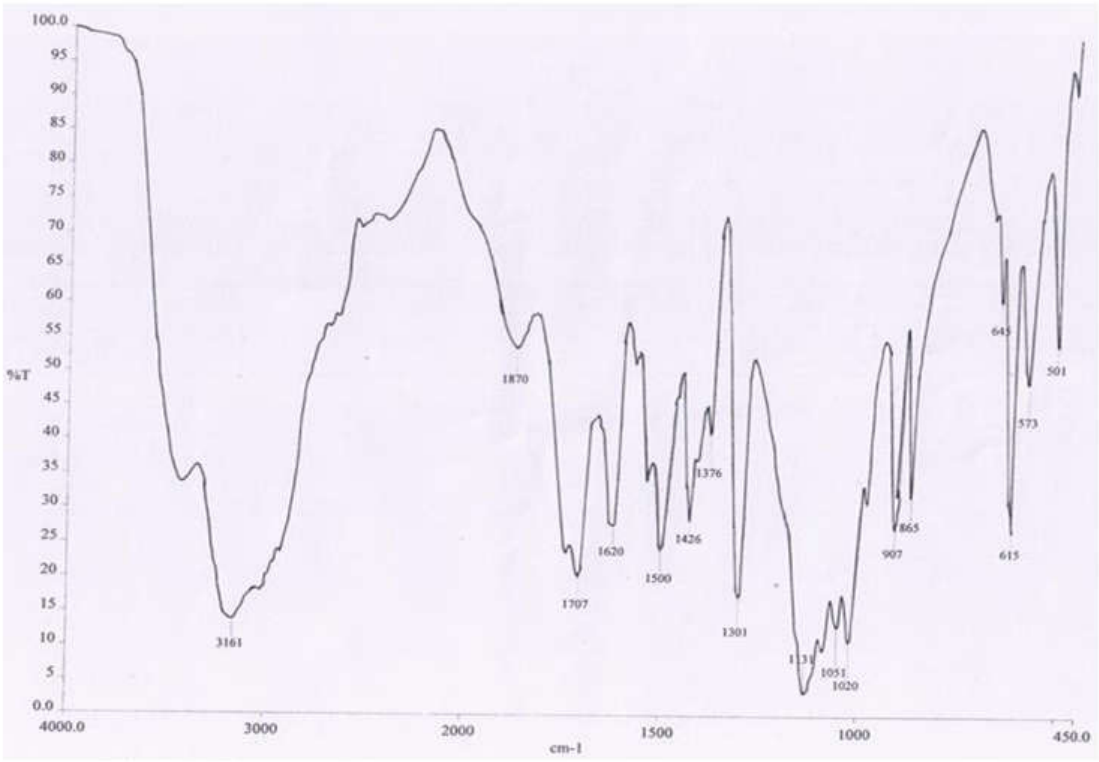

Figure 6. FTIR spectrum of L-proline doped TGS crystal

Thermal Properties

Thermogravimetric (TG) analysis, the differential thermal analysis (DTA) and the assessment of thermal changes by differential scanning calorimetry (DSC) was done at STIC, Cochin using TA instruments between 0°C to 700°C at a heating rate of 10°C / min in nitrogen atmosphere. The specimen was placed on aluminum non hermetic pans.

The temperature axis was calibrated by indium melting method. The recorded TG, DTA, DTG and TGA-DTA thermograms of L-PROLINE doped TGS crystals are displayed in Figures 7-10. These thermograms showed a major weight loss (-72%) in the temperature range between 242°C and 270°C, and 30% above 270°C. This can be attributed to the decomposition of glycine into CO_2 and NH_3. DTA curve reveled a sharp peak at 236.41°C corresponding to the decomposition of glycine.

Table 2. Assignment of FTIR frequencies (cm-1) L-proline doped TGS single crystals

Sl no.	Peak position (cm^{-1})	Assignments	TGS+5wt% L-proline
1	3164	NH str	3161
2	2369	Overtones	-
3	1869	Combinations	1870
4	1706	Ambide	1707
5	1622	NH_3+antisym b	1620
6	1505	NHib+NH_3 Sym b	1500
7	1425	CO_2 sym str+CH_2 tw	1426
8	1308	CH_2 tw+NHib	1301
9	1130	NC^2_2 str+NC^2_3 str	1131
10	1085	Aliphatic amines	1051
11	1019	NC^2_1 str+NC^2_1 str	907
12	906	C-C str	865
13	855	C_1H_2r + H_3r	645
14	615	C_2 ob+C_2 N t+C_1O ob	615
15	572	$V_4SO_4^-$	573
16	500	C_1N_1+N_2H ob	501

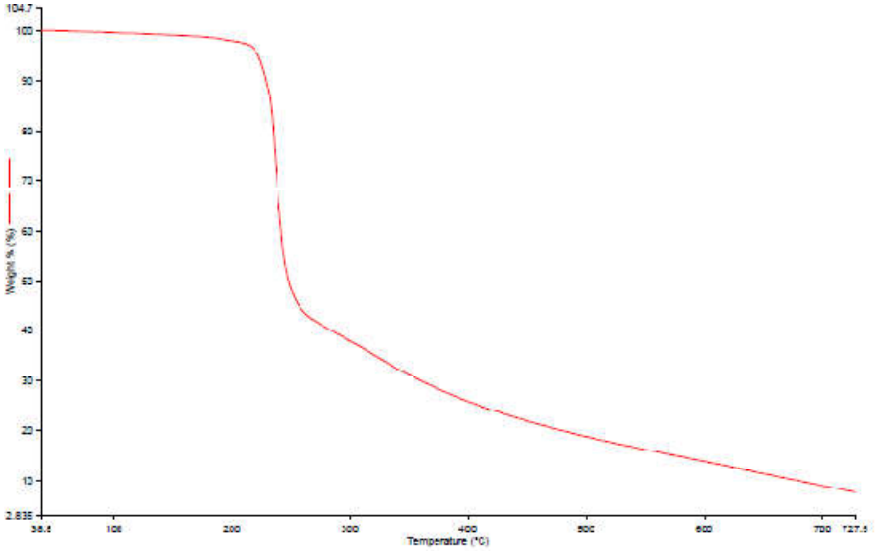

Figure 7. TG curve of L-proline doped TGS

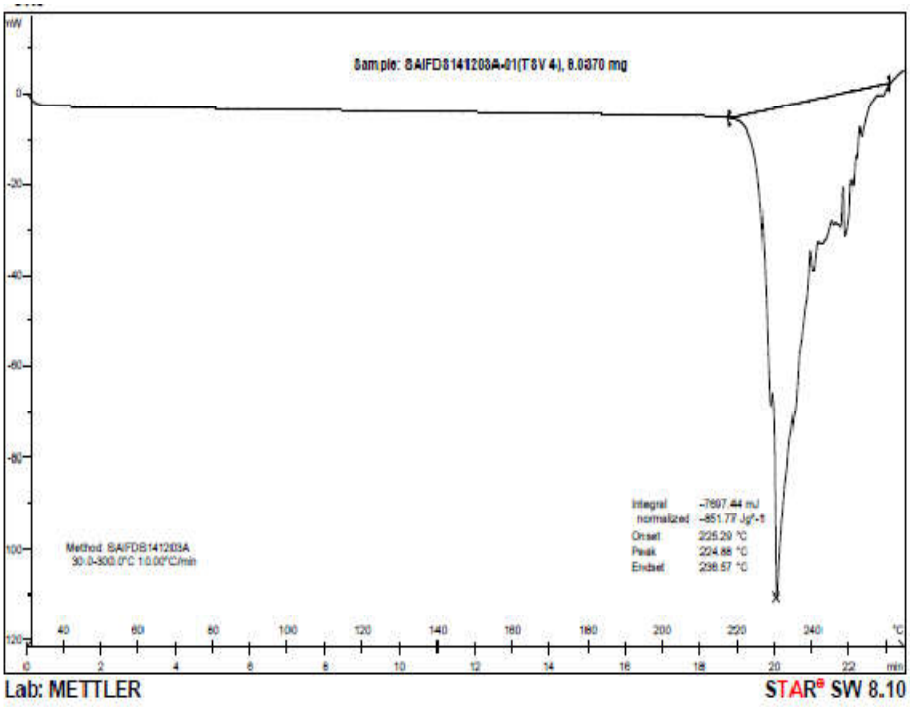

Figure 8. DTA Curve of L-proline doped TGS

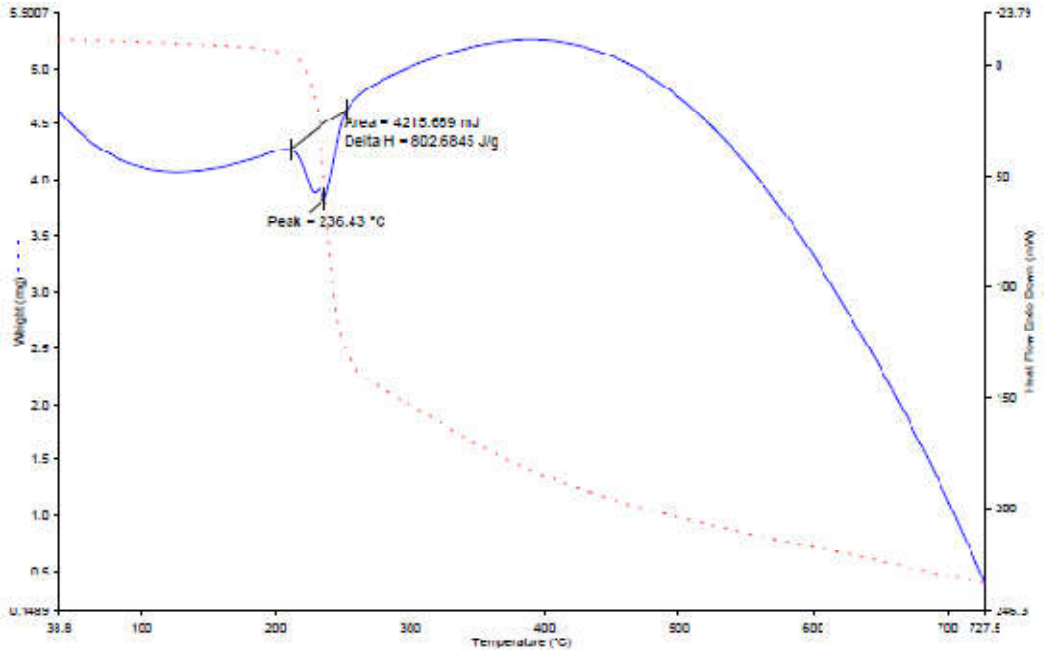

Figure 9. DSC Curve of L-proline doped TGS

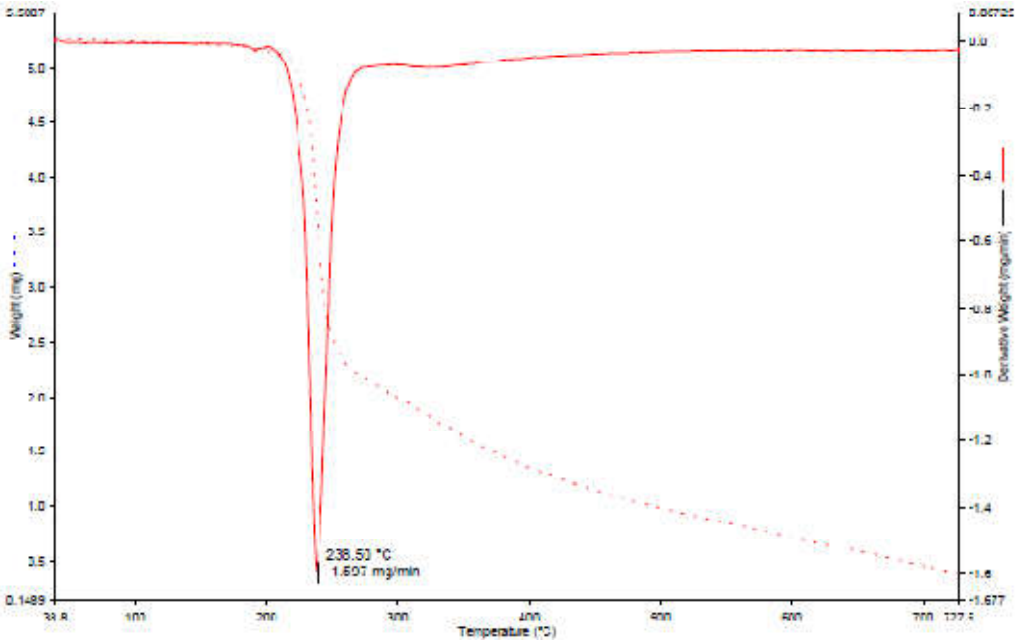

Figure 10. DTA-TGA Curve of L-proline doped TGS

Further increase in temperature resulted in the removal of H_2SO_4 in the form of H_2O and SO_3 with a total weight loss of 31 wt%. DTA curve of TGS also showed a broad endothermic peak around 437.3°C corresponding to the decomposition of sulphuric acid.

Conclusion

Analar Reagent (AR) grade of glycine, concentrated sulphuric acid ans L-proline were used for synthesis of samples. It is found that solubility of the samples increase with the increase in temperature. Density of the grown samples were determined by floatation method and found to be in good aggrement with literature value. Since the work hardening coefficient is found to be more than 1.6, all the grown crystals of this work are in the category of soft materials.

The grows crystals were supported by the transmittance spectrum showing 100% transmittance in the entire UV-Visible-NIR region. From single crystal XRD studies, the crystal structure and diffracting planes of the grown crystals have been identified. All the grown crystals of this work were found to crystallize in monoclinic structure. The unit cell parameters were found out. Various functional groups were identified from FTIR spectra. Thermal studies like Thermogravimetric and Differential Thermal Analysis (TG/DTA/DTG) studies shows that maximum decomposition occurs for all the samples in the range 250°-255°C.

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REFERENCES

Aravazhi S, Jayavel R and Subramanian C. 1997a. "Growth and stability of pure and amino doped TGS crystals" *Mater. Chem. Phys.* 50, 233-237

Aravazhi S, Jayavel R and Subramanian C. 1997b. "Growth and characterization of L-alanine and L-prolin doped triglycine sulphate crystals", *Mater. Res. Bull*. 32, 1503-1513

Arunmozhi G., Jayavel R., Subramanian C., 1997, "Growth and characterization of amino acid single crystals", Mater. Chem, Phys, 50, 57.

Beerman H. P., 1968, "Pyroelectric detector for infra red radiation", IEEE Trns. Devices 16, 554

Bhalla A.S., Fang C.S., X1.Y., Cross L.F., 1983, "Pyroelectric properties of the alanine and Triglycine sulphate (ATGSP)", Cross Appl. Phys. Lelf.43.932.

Bye K.L., whipps P.W., Keve E.T., 1972, "High internal Bias fields in TGS L-Alanine", Ferroelectrics, 4, 1972, 253.

Bye KL and Keve ET, 1972, "Structural inhibition of ferroelectric switching in triglycine sulphate. II, XIrradiation/field treatment". Ferroelectrics. 4, 87-95

Fang C.S., Yao X.I., Bhalla A.S., Cross L.E.,1983 "Pyroelectric Properties of Triglycine sulphate", Ferroelectrics 51, 9.

Jayaprakash Manoharan A. J., Joseph John N., Andavan P. 2011b, "Dielectric Properties of Proline doped Triglycine sulpho Phosphate (TGSP) Crystals", *Journal of Experimental Sciences,* 2(2), 33-35.

Jayaprakash Manoharan A. J., Joseph John N., Andavan P., 2011a, "Effect of amino acid doping on the dielectric properties of triglycine sulphate (TGS) crystals", Ind. J. of Sci. and Tech., 4,6, 688-691.

Joseph John N., Mahadevan C. K. 2008. "Studies on NaCl added ADP Single Crystals", Materials and Manufacturing processes, 23; 809-815.

Joseph John N., Selvarajan P., Benita Jeba Silviya S., Mahadevan C. K. 2007 , "Growth and characterization of Disodium Hydrogen Phosphate (DSHP) Single Crystals, Materials and Manufacturing processes, 22; 379-383.

Lineo M.E., Glass A.M., 1977, "Principles and Applications of ferroelectrics and Related materials", Clarendon Prens, oxford.

Meera K, Muralidharan R, Santhanaragavan P, Gopalakrishnan R and Ramasamy P, 2001, "Growth and characterization of L-cystine doped TGS crystals", *J. Cryst. Growth*. 226, 303-312

Mihaylova E and Stoyanov St., 1996, "Dielectric properties of rare earth doped TGS ", Phys. Status Solidi. 154, 797-802

Muralidharan R, Mohanakumar R, Ushasree PM, Jayavel R and Ramasamy P ,2002, "Effect of rare earth dopants on the growth and characterization of Triglycine sulphate", *J. Cryst. Growth* 234, 545.

Nakatani N ,1973, "Ferroelectric domain structure of Tri-Glycine sulphate observed using scanning electron microscope" Jpn. J. Appl. Phys. 12, 1723-1728.

Putley E. H. 1970, "Pyroelectric co-efficient and heat capacity of ferroelectric material TGS", Semimet. 5, 259.

Ravi G. Anbu Kumar S., Suhramanian C., Pillai P.K.C., Ranasamy P. 1995, "Studies on metal ions doped Triglycine sulphate single crystals", Ferroelectrics 165,47

Selvarajan P, Sivadhas A, Freeda TH and Mahadevan CK, 2008, Growth and Characterization of Trigyycine Sulfate crystals in water solubale subatances", *Physica B.* 403, 405.

Selvarajan P., Joseph John N., Mahadevan C. K., 2011, "Growth, Structural, Optical, Mechanical and Dielectric Characterization of Diammonium Hydrogen Phosphate (DAHP) single crystals" *Journal of Minerals and Material characterization and Engineering*, 10, 15, 1379-1389.

Sivakala P. and Joseph John N**.** and S. Perumal "Investigation on the Growth and Physio-Chemical Properties of L-Alanine Mixed BTCBC Single Crystals" *Int. Journal of Engineering Research and Applications, Vol. 4, Issue 7 (Version 4), July 2014, pp.145-151.*

Sivakala P. and Joseph John N. and S. Perumal "Investigation on the Growth and Physio-Chemical Properties of L-Alanine Mixed BTCBC Single Crystals" *Int. res. J. Eng. And Tech., 3,2,2016* , 1273-1278.

Theresita Shanthi T, Selvarajan P and Mahadevan CK, 2009, "Growth , Structural, Mechanical and Electrical properties of doped TGS", *Current Appl. Phys*. 9,1155.

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