International Journal of Materials Science ISSN 0973-4589 Volume 12, Number 2 (2017)

INVESTIGATION ON MECHANICAL, DIELECTRIC AND THERMAL PROPERTIES OF ALUMINIUM ION DOPED TGS SINGLE CRYSTAL

R.Raja[a], V.Santhanam[b], D.Vedhavalli[a] , P.Kurinji Nathan[a],

[a]*Department of Physics, SCSVMV University, Enathur, Kanchipuram -631561, India*
[b]*Department of Chemistry,SCSVMV University,Kanchipuram-631561, India*
Email- sridev_raja@yahoo.com

Abstract

TGS salt was synthesized by heating glycine (amino acetic acid) and concentrated sulphuric acid (H_2SO_4) in the ratio 3:1 at 500^oC. The salt was crystallized from water at room temperature by slow evaporation method. The parameters of the unit cell were determined by XRD technique. The vibrational frequencies of various functional groups in crystal has been derived from FT-IR analysis. UV-Vis spectral analysis showed the range and percentage of optical transmission. The thermal properties of grown crystal has been carried out by the TGA and DTA analysis. By Vickers microhardness method we analyzed the mechanical property of grown crystal.

Keywords: Ferroelectric crystals, XRD, FTIR, UV-Vis

INTRODUCTION

Among ferroelectrics, triglycine sulphate (TGS) crystal is an interesting ferroelectric material which shows second order ferroelectric phase transition at the Curie point. Below the *T*c, TGS possesses the polar point symmetry of group 2 of the monoclinic system[1]. 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 [2-3]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.

The TGS consists of SO_4^{2-}, 2($^+NH_3CH2COOH$) and $^+NH_3CH2COO$–species held together by hydrogen bonds. These bonds are easily broken by the polar molecules of water that explain the hygroscopicity of TGS. Along the *b*-axis, the SO_4 and layers are stacked alternately. The nearest two neighboring layers with identical chemical composition are rotated 180° around the *b*-axis against each other. In the present study, aluminium sulphate in various molar concentrations was doped with triglycine sulphate to improve the crystal properties.

SYNTHESIS OF TRIGLYCINE SULPHATE CRYSTAL

TGS salt was synthesized by taking AnalaR Grade (AR) glycine (NH_2CH_2COOH) 12.75 g and concentrated sulphuric acid (H_2SO_4, 98%) 4.3 mL, which corresponds to the molar ratio of 3:1, along with 50 ml of water, and the solution was heated up to 500^oC on thermostated bath to obtain a homogenous solution. The solution was allowed to evaporate at room temperature, which yielded colourless crystals of TGS due to super saturation. Glycine reacts with sulphuric acid as follows.

$$3(NH_2CH_2COOH) + H_2SO_4 \rightarrow (NH_2CH_2COOH)\ 3.H_2SO4$$

The seed crystals were harvested from the solution after four days and a suitable seed was selected. The selected seed was suspended in the freshly prepared solution. After a period of two weeks, optically transparent defect free crystals were obtained from the mother solution. The synthesized salt was again dissolved in double distilled water and then recrystallized by natural evaporation process[4]. This process was repeated two times to improve the purity of the material.

GROWTH OF ALUMINIUM SULPHATE DOPED TRIGLYCINE SULPHATE CRYSTAL

A 1.0 mL and 0.2 mL portions of 1M of $Al_2(SO_4)_3$ solution was added to 100 mL of two different portions of the saturated solution of TGS to obtain $Al_2(SO_4)_3$ doped TGS crystals. This solution was stirred well for 60 minutes and filtered out to remove the undissolved particles. The filtered out solution was kept covered with perforated sheet and it is subjected to slow evaporation at room temperature. The grown crystals were as shown in figure 1 and 2.

Figure 1. crystal of 1 % $Al_2(SO_4)_3$ doped TGS

Figure 2. crystal of 0.2 % $Al_2(SO_4)_3$ doped TGS

RESULTS AND DISCUSSION

X-Ray Diffraction Studies

The molecular geometry and intermolecular interactions can be analyzed by single crystal X-Ray diffraction study. The BRUKER NONIUS CAD4 single crystal X-ray diffractometer was used to find the lattice parameters of the grown crystal. The lattice parameter value has been evaluated and it indicates that the pure TGS, 0.2% $Al_2 (SO_4)_3$ doped TGS and 0.1% $Al_2 (SO_4)_3$ doped TGS have monoclinic system. From the results it was seen that small variations in lattice parameter of grown crystal due to presence of dopant in the crystal. The lattice parameter values are shown in table 1

Table 1: lattice parameters of $Al_2 (SO_4)_3$ doped TGS crystals

Lattice parameters	**Pure TGS (From reported)**	**0.2% $Al_2 (SO_4)_3$ doped TGS**	**1% $Al_2 (SO_4)_3$ doped TGS**
a(Å)	9.601	9.135	9.124
b(Å)	12.560	12.638	12.563
c(Å)	5.450	5.718	5.727
β°	110.36	105.91	105.56
V(Å)^3		635.1	631.3

FTIR Spectral Analysis

The spectra were recorded in the wavelength range 400- 4000 cm^{-1}. The characteristic absorption peaks observed in the range from 400-4000 cm^{-1} are shown in figure 3.The pure TGS crystal shows a broad and strong absorption band in the range 2380 - 3800 cm^{-1} for the O-H stretching of hydrogen bounded carboxyl groups and the N-H stretching NH_3^+ group. The C=O stretching vibration of carboxyl group appears as a sharp band at 1620 cm^{-1}. The C-H bending vibrations appear at 1500cm^{-1}. The N-H bending vibrations are present at 1423cm^{-1}. The asymmetric S=O stretching frequencies can be assigned to frequency 1300 cm^{-1}. A strong band at 1130 cm^{-1} arises from C-O stretching. The transitional oscillations of NH_3^+ groups appear at 617, 574 and 501.5 cm^{-1}. All these details are reported in literature [5]. The FTIR spectra of 0.2 mole $Al_2 (SO_4)_3$ doped TGS, 1 mole% $Al_2 (SO_4)_3$ doped TGS shows similar features as that of undoped TGS spectrum. The observed frequencies and their assignments for $Al_2 (SO_4)_3$ doped TGS crystal are compared with those of pure TGS and listed in Table 2.

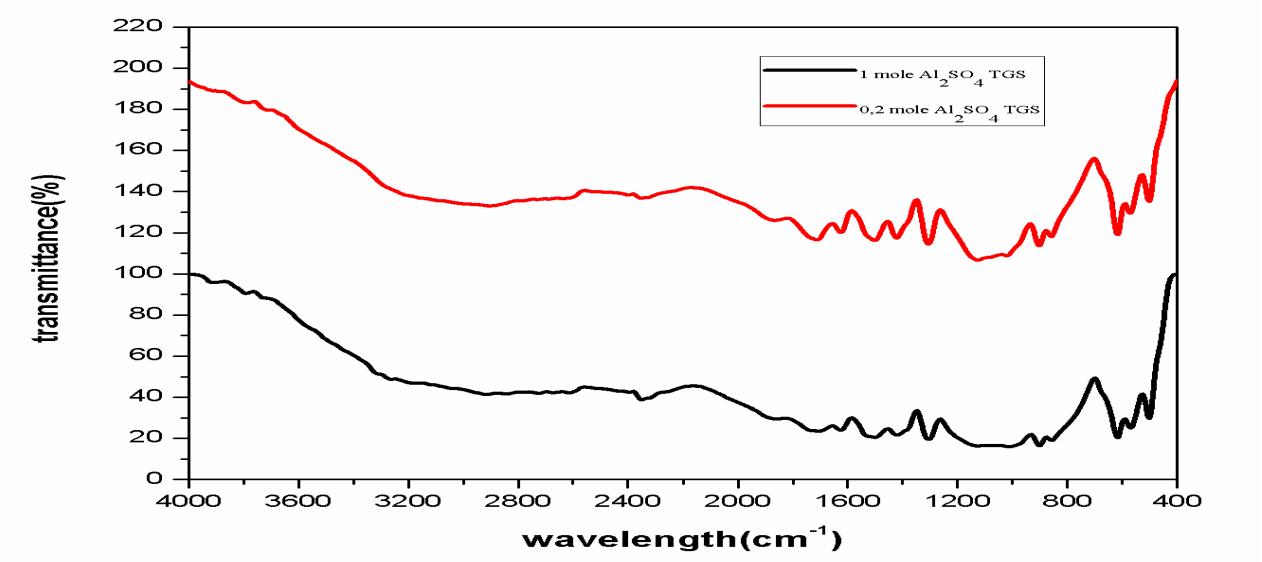


Fig.3. FTIR spectrum of $Al_2 (SO_4)_3$ doped TGS crystals

Table 2: FTIR spectral assignments of pure and $Al_2(SO_4)_3$ doped TGS crystals

Wavenumber (cm^{-1})			**Vibrational Band Assignments**
Pure TGS (from reported)	0.2 mole% $Al_2 (SO_4)_3$	1 mole% $Al_2 (SO_4)_3$	
2638 2391	2726 2351	2905 2352	CH_2 stretching
1859	---	1867	(NH_3^+) asymmetric bending
1712	1707	1712	Overtones and combinations
1627	1625	1624	C=O stretching of COOH
1496	1501	1501	($NH3^+$) asymmetric bending
1419	1420	1421	NH_4 bending+ NH3 symmetric bending
1303	1305	1305	asymmetric S=O stretching / CO2 symmetric stretching + CH2 twisting
1126	---	1126	NC_2^{α} stretching + NC_3^{α} stretching
1018	1014	1020	SO_4 vibrations
902 856	901 856	901 858	C-C stretching
570	569	570	NH_3^+ torsional oscillations
501	501	501	NH_3 oscillation

UV-Visible Analysis

The UV-Visible spectrum was recorded using SHIMADZU UV-spectrometer 1601 in the range of 200- 1000 nm [6]. The recorded absorption spectrum is shown in figure 4. From the spectrum, it is observed that the crystal has a lower cutoff wavelength in the vicinity of 313nm in 0.2 % $Al_2(SO_4)_3$ doped TGS and 321nm 1 % $Al_2(SO_4)_3$ doped TGS. After the cutoff wavelength, there is no absorption in visible region.

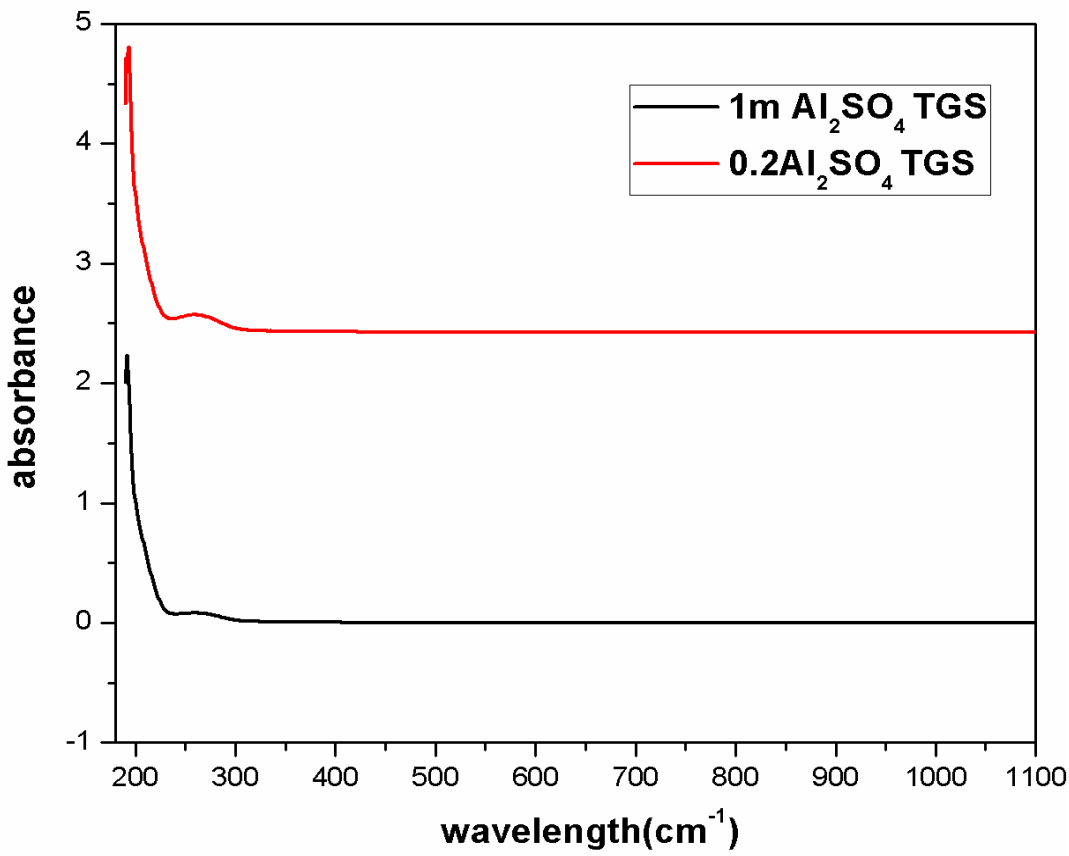


Figure 4. UV-Visible spectrum of $Al_2 (SO_4)_3$ doped TGS crystals

Thermal Analysis

To study the thermal stability of grown crystal, the DTA/TGA analysis were carried out between0 to 730^oC for 0.2 % $Al_2 (SO_4)_3$ doped TGS and 0 to 630 ^oC for 1 % $Al_2 (SO_4)_3$ doped TGS. In the nitrogen atmosphere at heating rate 10 ^oC/min using NETZSCH STA 409 C/Cd thermal analyzer. The recorded spectra of the 0.2 % $Al_2(SO_4)_3$ doped TGS and 1 % $Al_2(SO_4)_3$ doped TGS are shown in figures 5 and 6 .

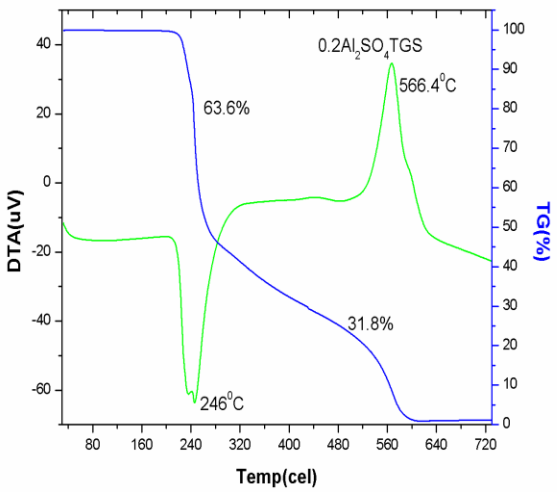


Fig .5 TGA / DTA curve of 0.2%

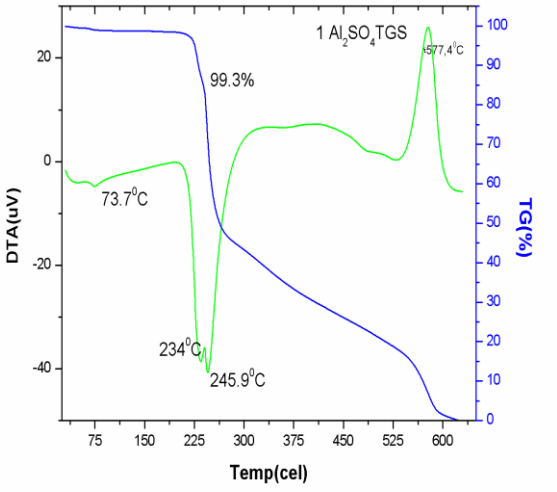


Fig .6 TGA / DTA curve of 1.0% doped TGS crystals

For 0.2 % $Al_2 (SO_4)_3$ doped TGS crystals, the initial mass of the material subjected to analysis was 6.607 mg and the final was only 1.129% of the initial mass at temperature of about 730 ºC [7-8]. From the TGA curve, the thermal stability of the sample is realized up to 194 ºC and there after the materials show loss in weight due to molecules, which are loosely bounded to the metal ion. The major 63.6% of weight loss between 209 ºC to 430 ºC is due to the liberation of volatile substances. It was observed from DTA curve, that the material undergoes exothermic transition at about 246 ºC where the decomposition starts. The material is fully decomposed at an irreversible endothermic transition at about 566 ºC. It is inferred that the melting point of the material takes place in the vicinity of 246 ºC. The sharpness of the endothermic peak shows good degree of crystallinity of the grown 0.2 % $Al_2 (SO_4)_3$ doped TGS.

For 1 % $Al_2 (SO_4)_3$ doped TGS crystals, the initial mass of the material subjected to analysis was 5.727 mg and the final was only 0.0322% of the initial mass at temperature of about 630 ºC. From TGA curve, the thermal stability of the sample is stable up to 183 ºC and there after this material also show weight loss due to molecules, which are loosely bounded in metal ion. The major 99.3% of weight loss in the temperature range between 209 ºC to 614 ºC.

From DTA curve, the material undergoes three exothermic transitions. The first exothermic peak at 73.7 ºC indicates the melting point of the grown crystal. The crystal has second exothermic peak at 234 ºC and third exothermic peak at 245.9 ºC. The materials have endothermic transition at about 577 ºC. . The sharpness of the endothermic peak shows good degree of crystallinity of the grown 1% $Al_2 (SO_4)_3$ doped TGS.

Dielectric Analysis

Crystals of 0.2 % $Al_2 (SO_4)_3$ doped TGS and 1 % $Al_2 (SO_4)_3$ doped TGS were selected to measure dielectric permittivity, dielectric loss and A.C conductivity using HIOKI 3532 -50 LCR HITESTER model 3532-50 LCR meter in the frequency range of 50 Hz and 5MHz at

various temperatures [9-10]. The dielectric constant and dielectric loss of the samples were calculated from capacitance and dissipation factor. The dielectric constant of the 0.2 % $Al_2(SO_4)_3$ doped TGS and 1 % $Al_2(SO_4)_3$ doped TGS crystal were calculated through the capacitance by the fundamental equation (1)

$$\varepsilon_r = \frac{Cd}{\varepsilon_o A} \qquad (1)$$

Where C is capacitance is thickness of the sample, $\varepsilon_o = 8.854 * 10^{-12} Fm^{-1}$ is the permittivity of free space, A is the area of cross section

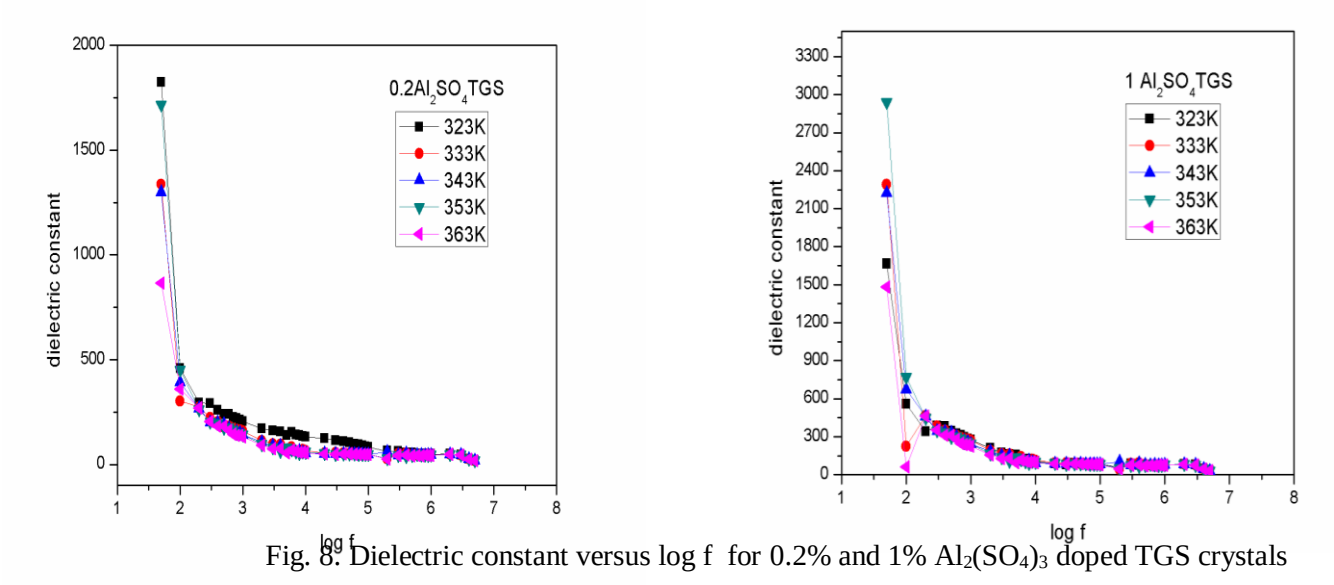


Fig. 8: Dielectric constant versus log f for 0.2% and 1% $Al_2(SO_4)_3$ doped TGS crystals

The dielectric loss[11] (tan δ) were calculated by the equation (2)

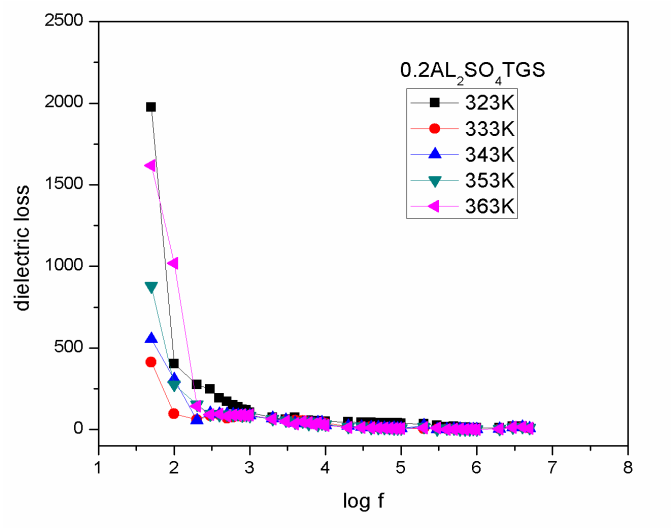
$$\tan\delta = \varepsilon_r D \qquad (2)$$

Where, D is the dissipation factor. The variation of dielectric constant was measured as a function of frequency at different temperatures for both crystals shown in Figure 8, while the corresponding dielectric losses are depicted in Figure 9 & 10. The very high values of and tan δ at low frequencies are due to presence of all the form of polarizations namely, space charge, orientation, ionic and electronic popularization. As the frequency increases, the space charge cannot sustain and comply with external field and hence the polarization decreases. According to miller rule, the low value of dielectric loss at high frequency reveals the high optical quality of the crystal.

The AC conductivity[12] is calculated using

$$\sigma_{ac} = \omega \varepsilon_o \varepsilon_r \tan\delta \qquad (3)$$

Where, f is the frequency of the applied electric field. The figure 11 and 12 shows the variation of ac conductivity for different frequencies. From the graph, it is observed that both the crystals have the AC conductivity feebly increases up to the logarithmic of 6.30Hz. From the sharp increases, it was observed in the logarithmic frequency 6.47Hz indicates the dielectric breakdown frequency of the material.



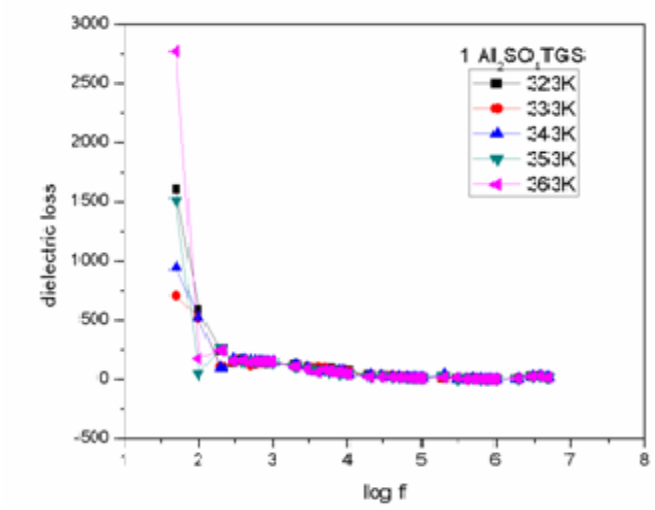
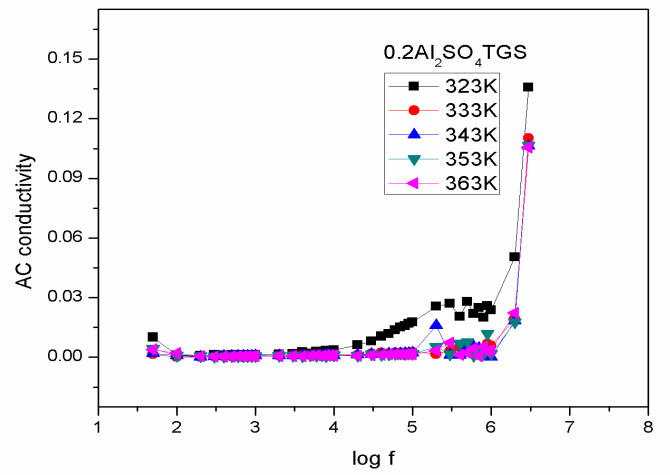
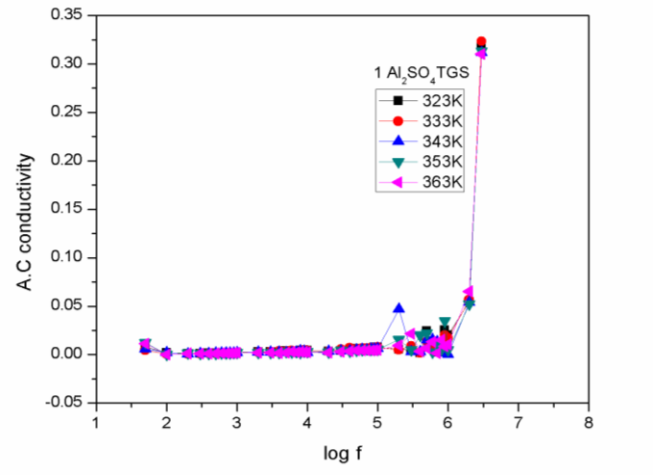


Figure 9. dielectric loss vs log f for
Figure 10. dielectric loss vs log f for 0.2% $Al_2(SO_4)_3$ doped TGS crystals
1% $Al_2(SO_4)_3$ doped TGS crystals

Figure 11.AC conductivity vs log f

Figure 12 AC conductivity vs log f





for 0.2% $Al_2(SO_4)_3$ doped TGS crystals

for 1% $Al_2(SO_4)_3$ doped TGS crystals

Microhardness Studies

Vickers microhardness indentations were made on as grown crystal surface of the 0.2 % $Al_2 (SO_4)_3$ doped TGS and 1 % $Al_2 (SO_4)_3$ doped TGS crystals at room temperature with the load ranging from 25 g, 50 g and 100 g using Vickers microhardness tester[13]. There were two trials made for each indentation. Time of indentation was kept at 5 seconds for all trials. The Vickers hardness number was calculated using the expression

$$Hv = \left[\frac{1.8544\ P}{d^2}\right] kg/mm^2 \qquad (4)$$

Where, H_V is the Vickers hardness number in kg/mm^2, P is the applied load in kg and d is the diagonal length of indentation impression in millimeter and 1.8544 is a constant of a geometrical factor for the diamond pyramid. A plot obtained between the hardness number and the load is depicted in Figure 13.

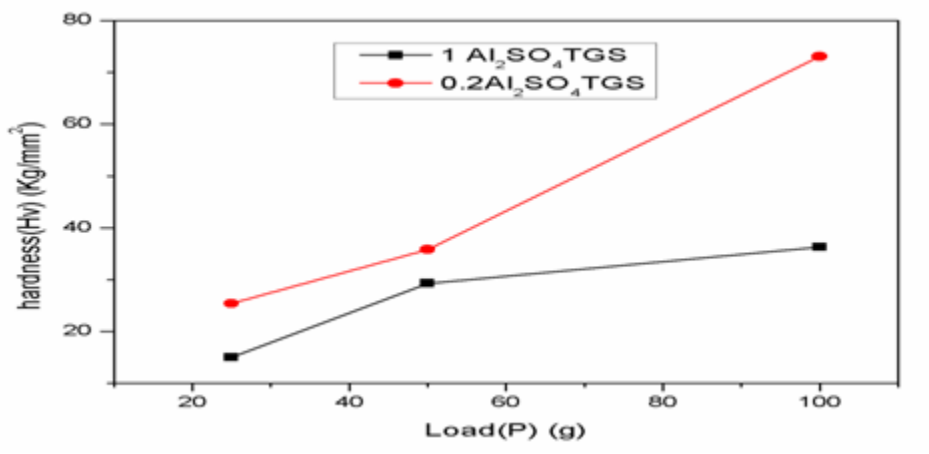


Figure 13. Variation of Hv with applied load for $Al_2 (SO_4)_3$ doped TGS crystals

Mayer Index (N)

Kick law proposed the relation between load P and indentation length d[14] is given by,

$$P = k_1\, d^n \qquad (5)$$

Where, n is the Mayer's index or work hardening coefficient which is found out from the slop of the plot of log P and log d gives a straight line as shown in Figure 14 and k_1 is the standard hardness, which is found by the intercept. In the present investigation, the work hardening coefficient (n) for 0.2 % $Al_2 (SO_4)_3$ doped TGS and 1 % $Al_2 (SO_4)_3$ doped TGS crystals are n = 2.722 and 1.172.

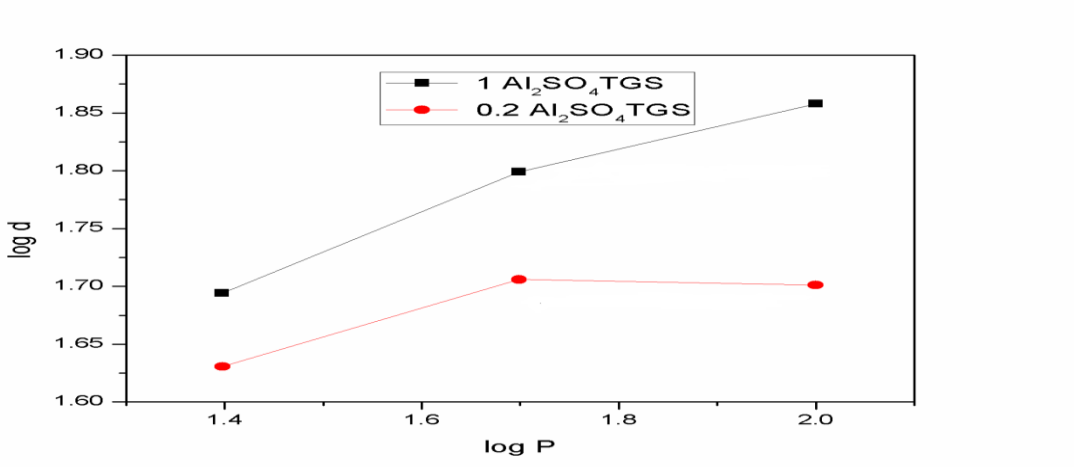


Figure 14 Log P versus log d

CONCLUSION

Triglycine sulphate (TGS) exibits ferro electric properties and have been investigated in the recent decades. In the present work 0.2 % $Al_2 (SO_4)_3$ doped TGS and 1 % $Al_2 (SO_4)_3$ doped TGS crystals were grown by slow evaporation method. The grown crystals were characterized by UV-Vis spectra, FT-IR, single XRD, TGA/DTA, dielectric and Vickers micro hardness studies.

The grown crystals of pure TGS, 0.2 % $Al_2 (SO_4)_3$ doped TGS and 1 % $Al_2 (SO_4)_3$ doped TGS subjected to single crystal X-ray diffraction studies revealed that all crystals belongs to monoclinic system. FTIR analysis identifies the presence of functional groups which absorb at definite frequencies. It is evident that Vickers hardness number increases with increasing load. From TGA/DTA analysis, the melting points and stability of the crystals were calculated. The low value of dielectric constant and dielectric loss at high frequencies is important for the device applications.

REFERENCES

[1] Sun, X., Wang, M., Pan, Q. W., Shi, W., and Fang, C. S., "*Study on the Growth and properties of Guanidine Doped Triglycine Sulfate Crystal*",(1999), *Crystal Research and Technology*, Vol.**34**, pp.1251-1254.

[2] R. Raja, S. Seshadri, T. Gnanasambandan, R.R. Saravanan, "*Crystal Growth and Properties of NLO Optical Crystal –ButylatedHydroxyToluene (BHT)SpectrochimicaActa Part A: Molecular and Biomolecular Spectroscopy*.

[3] Renugadevi, R. Kanchana, G. Kesavasamy, R.,"*Growth and Characterization of Triglycine (TGS) Single crystals*", (2013), Elixir crystal growth vol. **55A** (2013), p 13033-13035.

[4] Alexandru ,H.V, "*Pure and Doped Triglycine Sulfate Crystals Growth and Characterization*", (2009), Interdisciplinary Transport Phenomina:Ann.N.Y. Acad. Sci. 1161:387-396.

[5] Wooster, W.A., "*Physical properties and atomic arrangements in crystals*", (1953), Rep. Progr. Phys. Vol.16, p.62-82. Matthew, F.B.; Jos, O.; Richard, J.S.; Williams, E.R. J. Am. Chem. Soc. 2008, **130**, 6463.

[6] FarhanaKhanum, JibanPodder, "*Structural and optical properties of Triglycine Sulfate single crystals doped with potassium Bromide" Journal of crystallization process and technology,* 2011,1, p-26-31.

[7] Theresita S.N.; Selvarajan P.; Mahadevan, C.K., *J. Curr. Appl. Phys*. 2009, **9**, 1155.

[8] Sivanesan, G.; Kolandaivel, P.; SelvasekaraPandian, S. *J. Mater. Chem. Phys*. 1993, 34, 73.

[9] Srinivasan, M.R.; Bhat, H.L.; Narayanan, P.S. *Ferroelectrics*. 1983, **46**, 191.

[10] Eisner, *J. Ferroelectrics*. 1978, 17, 575.

[11] Ragahvan, C. M., Sankar, R., Mohankumar, R., and Jayavel, R., (2008),"*Effect of amino acid doping on the growth and ferroelectric properties of triglycinesulphate single crystals",* (2008), *Mater. Res. Bull.*, Vol.**43**, pp. 305 -311.

[12] Farhana Khanum, Jiban Podder, " *Synthesis, Growth, Electrical Transport Properties of pure and $LiSO_4$- Doped Triglycine Sulphate crysta*l", 2012, International J. of Optics, p 797-803.

[13] Onitsch, E. M., (1947), "*Micro-hardness Testing*", *Mikroscopie*, Vol. **2**, pp.131-151.

[14] Meyer, E.,"*UntersuchungenüberHärteprüfung und HärteBrinellMethoden*,", (1908), *Z. Ver. deut.Ing*., Vol.**52**, pp.645-654.