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IR and Raman Spectral Studies of Pure and Doped TGSZC Crystals

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ABSTRACT

Glycine family crystals are very useful materials for electronics and many optical applications. In present work single crystals of pure and ADP-, KDP- (0.2 mol) doped Triglycine sulpho zinc chloride (TGSZC) crystals are grown by solution growth method. Grown crystals are characterized by UV-Vis, IR and Raman spectral studies. From UV –Vis spectra optical quality of all crystals is determined. From IR and Raman spectra characteristic vibrations are identified. Powder XRD study reveals the Crystal structure of grown crystals. Ferroelectric nature of all crystals is tested using homemade Sawyer-Tower circuit. Electrical conductivity measurements are carried out for pure and doped TGSZC crystals.

Introduction

Triglycine sulfate is a room temperature ferroelectric crystal and belong to Pyroelectric family. It exhibits order-dis order phase transition at the Curie point 49^0c. The crystal structure of TGS was reported by Hoshino et al [1]. The unit cell of TGS contains three types of glycines GI, GII, and GIII [2]. Glycine I is in the form of Zwitter ion. GII and GIII are two planar glycines. They have protonated Carboxyl groups which have taken protons from the sulfuric acid. They form chain like system with SO_4^{2-} group. Such configuration of TGS is regarded as particularly important for the ferroelectric behavior of TGS crystal. The orientation of positively charged NH_3 groups determines the direction of spontaneous polarization in TGS. The spontaneous polarization reversal in TGS is due to the proton transfer between glycine and glycinium ions. TGS exhibits order-disorder phase transition at the Curie point [3]. Above Curie temperature it is in para electric phase with space group symmetry $P2_1$ /m and below Curie it is in ferroelectric phase with space group symmetry $P2_1$ with two formula units per unit cell. The unit cell parameters of TGS are a = 9.15A˚, b = 12.6445A˚, c = 5.725A˚ and β = 105.53˚ [4]. The domain structure of TGS was investigated by C.Berbecaru et al in 20004 and reported that in TGS majority of domains were found in the form of rod shaped with lenticular cross sections elongated in the direction perpendicular to C-axis. M.R.Posledovich and M.Malyarevich in 1996 had reported that TGS provides rich lattice vibration spectrum below 300 cm^{-1}. The main disadvantage of TGS is its lower Curie temperature and easy depolarization by time, electrical, mechanical and thermal means. Because glycine has no asymmetric carbon and it is optically inactive. It is believed that doping of TGS with an optically active molecule will keep permanent polarization in TGS lattice. There are a large number of researches going on TGS to minimize the depolarization effect and to keep permanent polarization in TGS lattice. H.J.Byrne et al (2000) had reported that there is no change in crystal structure for N_d doped TGS and N_d is coordinated with glycine. But in the case of ADP (S.Lanceros Mendez et al in 2002), L-Asparagine (M. Beatrice Margaret et al in 2002) and L-tryptophan (D.Jayalakshmi and J.Kumar in 2008) doped samples change in crystal morphology is observed. Tc value is higher for l-threonine, dl-threonine, l-methionine (K.Meera et al in 2004) doped TGS and TGSP (Aparna Saxena et al in 2004) crystals. Spectral investigation of TGS doped with ADP (S.Lanceros Mendez et al in 2002), L-tryptophan (D.Jayalakshmi and J.Kumar in 2008), Phosphoric acid (Aparna Saxena eta l in 2004), L-lysine (W.Kulita and M.Trybus in 2003), L-Cystine (K.Meera et al in 2001), reveals that doped samples have lower Spontaneous polarization values Ps and higher coercive field values compared to pure TGS. Higher Coercive field value implies that the crystal is in mono domain state. Pyroelctric coefficient is increased for Thiourea (R.Muralidharan et al in 2004), L-alanine and DL-alanine (C.Berbecaru et al in 2005), L-lysine (Youpping He et al in 2000) doped samples. Incorporation of Nitric acid (R.Parimaladevi and C.Sekar) and EDTA (K.Meera et al in 2005) into TGS crystal increases the dielectric constant value. The substitution of amino acids l-threonine, dl-threonine, l-methionine (K.Meera et al in 2004) and L-Cystine (K.Meera et al in 2001) results in the decrease of dielectric constant value compared to pure TGS crystal. Zinc chloride (A.Wojciechowski et al in 2010) and Urea (S.Sivakumar et al in 2009) doped samples exhibit Non-linear optical property and have S.H.G efficiency much higher than standard KDP crystal. In case of LGLM (T.Bharthasarathi et al in 2009), La, Ce, Nd (R.Muralidharan et al in 2002), L-lysine (Youping He et al in 2000) doped TGS crystal strong internal bias field is created indicates that the dopant is reduced the depolarizing effects in TGS crystals. The internal bias field fixes the polarization in a preferential direction with minimum possibility of polarization reversal . Doping of TGS with metal ions Fe^{3+}, Cr^{3+} and Co^{2+} decreases the indirect band gap (A.Abu El Fadl in 1999). Investigation of TGS samples previously influenced by electric field E perpendicular to ferroelectric b axis reveals that there are rigid stripped domains parallel to c

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axis (C.Cwikiel et al in 2000). Vickers microhardness study reveals that hardness value is increased for TGS when doping with L-lysine (R.Mohan kumar et al in 2001) and Imino diacetic acid (Chitharanjan Rai et al in 2010). But hardness value of crystal is decreased by doping TGS with l-threonine, dl-threonine and l-methionone (K.Meera et al in 2004), L-Cystine (K.Meera et al in 2001), Thiourea (R.Muralidharan et al in 2004), and EDTA (K.Meera et al in 2005). In present work pure and ADP-, KDP- (0.2 mol) doped TGSZC crystals are grown from solution. Both of the dopants are good non- linear optical and electro-optical materials. ADP possesses excellent dielectric, piezoelectric, Antiferroelectric, electro-optic and non-linear optical property. ADP is most widely used in the field of Optics due to birefringence property. KDP is also a ferroelectric material and good Nonlinear optical material. In present work Antiferroelectric ADP and ferroelectric KDP are doped with TGSZC crystal in order to enhance its optical as well as ferroelectric nature.

2. Crystal growth and characterization

Pure and ADP-, KDP- (0.2 mol) doped TGSZC crystals are grown by solution growth method (K.Meera et al in 2000). Pure TGSZC crystal is grown by taking 3 moles of Analar grade Glycine, 0.5 mol of Sulphuric acid and 0.5 mol of Zinc Chloride in 100 ml of distilled water. The solution is stirred well for 3 hrs. Then the solution is filtered and allowed to slow evaporation. ADP and KDP (0.2 mol) doped crystals are grown by the same method. Good quality crystals are obtained within the growth period of 1- 3 months. Grown crystals are shown in Fig. 1.

Fig. 1 Grown crystals of pure and ADP-, KDP- (0.2 mol) doped TGSZC.

UV-Vis absorption spectra of grown crystals are recorded in the wavelength range from 200-800nm using UV-Vis 2450 Make Shimadzu model spectrophotometer. FT-IR spectra are recorded in the frequency range from 400-4000cm^{-1} using IR Affinity Make Shimadzu model spectrophotometer. FT-Raman spectra were recorded in the frequency range from 0-3500cm^{-1} using the excitation radiation of 5145A° using Lab Ram HR 800 model spectrophotometer. Power XRD pattern of grown crystals is recorded using BRUKER diffractometer with CuKα radiation (λ = 1.054A°). Ferroelectric hysteresis study is carried out using home made Sawyer-Tower circuit (C.B.Sawyer and C.H.Tower in 1930). Electrical conductivity measurements are carried out using IMPEDENCE ANALYSER IM3570.

3. Results and discussion

3.1 UV-Vis spectral investigation of grown crystals

Fig. 2 shows UV-Vis absorption spectra of pure and ADP-, KDP- (0.2 mol) doped TGSZC crystals. For TGSZC crystal, λ_{max} = 232.5nm. For TGSZC+ADP, λ_{max} = 232nm and for TGSZC+KDP, λ_{max} = 232nm. For doped crystals there is slight shift in wavelength of maximum absorption λ_{max}. This is referred to as hypsochromic shift. From this it is observed that there is change in energy levels to effect transition. For doped samples the energy required to effect the electron promotion is higher compared to pure TGSZC. So that the wavelength that provides this energy is decreased for doped crystals. Absorption at lower wavelength reveals that there must be higher energy transition corresponding to C = C – NO_2 group. It is observed that all these crystals have transmission percentage of above 90%. Energy band gap values were found out using the relation E = 1240/ λ_{max} eV (J.Balu et al in 2009). Also Energy band gap values are obtained from Urbach plot and results are shown in table 1.

Table 1 Energy band gap values of grown crystals

Crystal	Eg (calculated from Eg = 1240/λ_{max} eV) eV	Eg (obtained from Urbach Plot) eV
TGSZC	5.33	5.1606
TGSZC+ADP	5.34	5.1729
TGSZC+KDP	5.34	5.1496

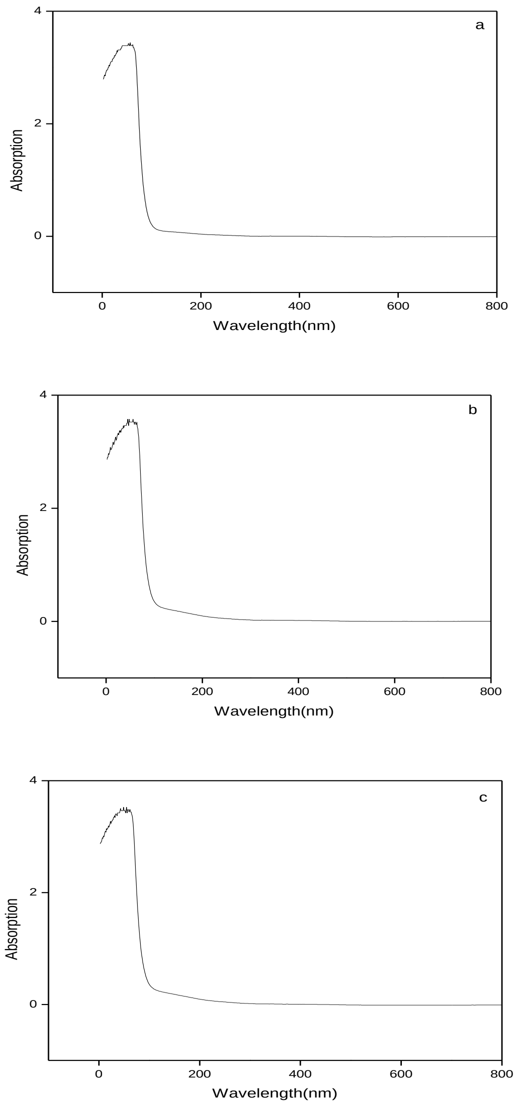


Fig. 2 UV-Vis absorption spectra of a)TGSZC b) TGSZC+ADP c) TGSZC+KDP crystals.

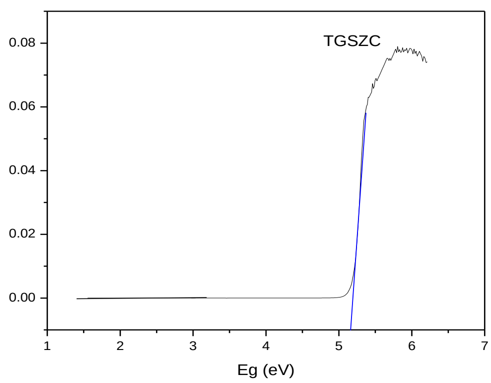


Fig. 3a

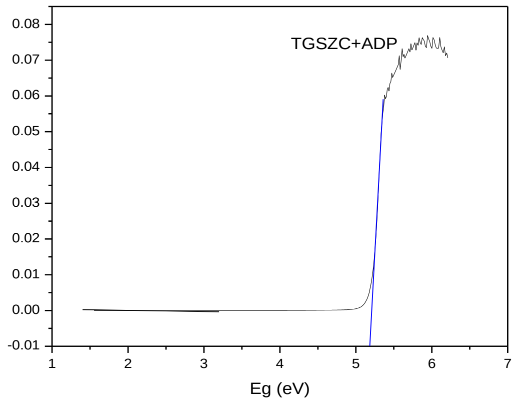


Fig. 3b

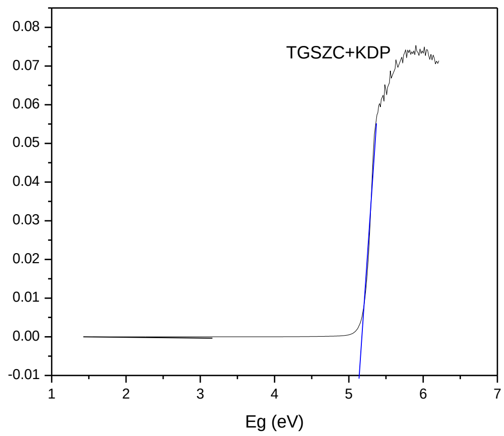
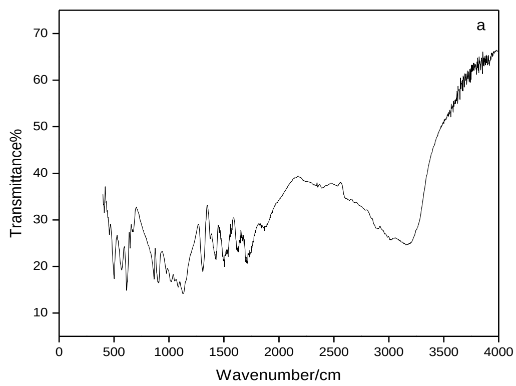
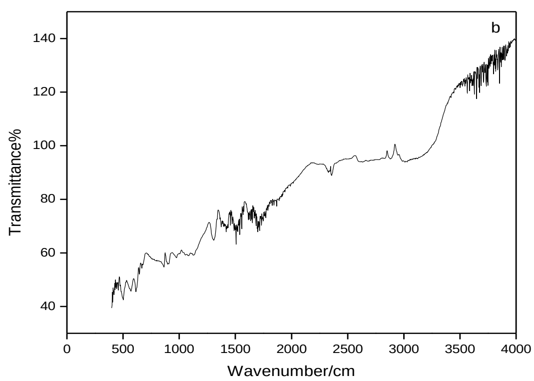


Fig. 3c

Fig. 3 Urbach plot of a) TGSZC b) TGSZC+ADP c) TGSZC+KDP crystals.





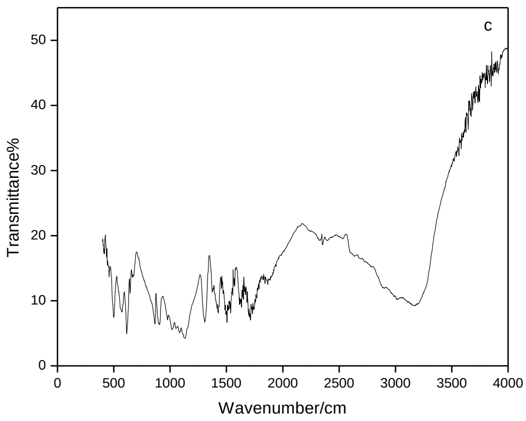


Fig. 4 FT-IR spectra of a)TGSZC b) TGSZC+ADP c) TGSZC+KDP crystals.

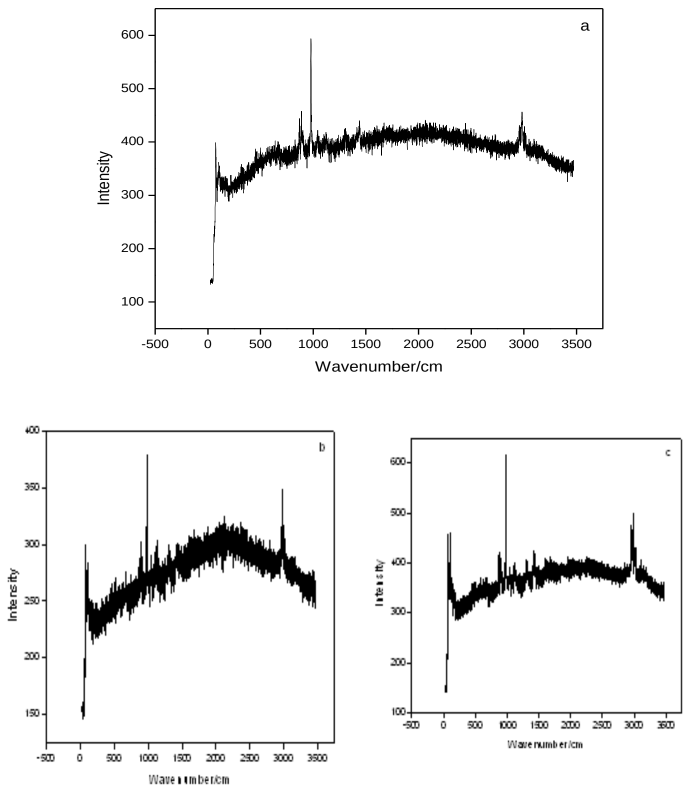
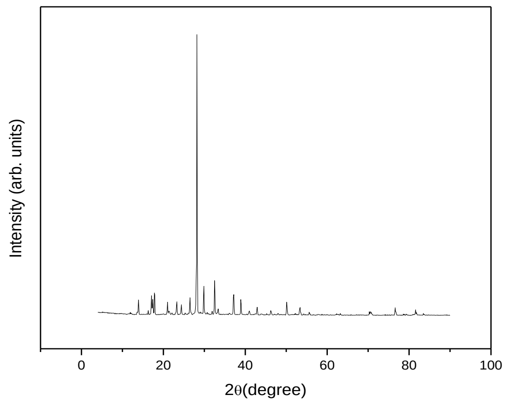


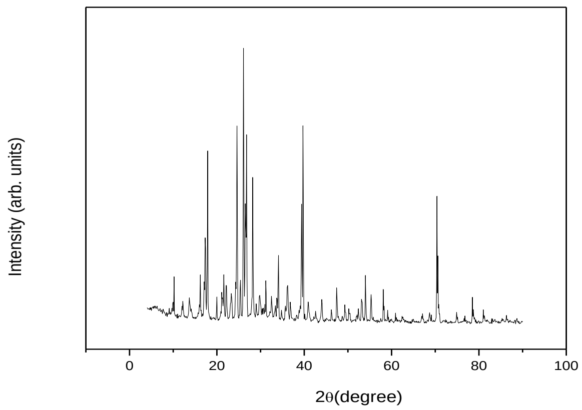
Fig. 5 FT-Raman spectra of a)TGSZC b) TGSZC+ADP c) TGSZC+KDP crystals.

3.2 FT-IR spectral analysis

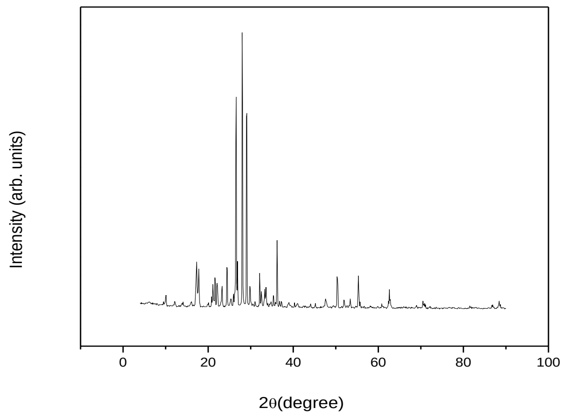
Fig. 4 shows FT-IR spectra of pure and ADP-, KDP- doped TGSZC crystals. FT-IR spectrum of pure TGSZC crystal matches very well with the earlier reported values of pure TGS crystal (R.Parimaladevi and C.Sekar). All expected characteristic vibrations are observed and assignments were tabulated in Table 2. IR band at 1429 cm^{-1} and 1622 cm^{-1} corresponding to symmetric and asymmetric stretching vibrations of COO^{-} indicate the Zwitter ion configuration of glycine (R.Parimaladevi and C.Sekar). IR bands observed in the region between 1683 cm^{-1} to 1869 cm^{-1} corresponding to stretching vibration of C = O indicate the presence of glycinium ion configuration (R.Parimaladevi and C.Sekar). Degenerate modes of NH_3 bending and C = O, NH_4 , C – H, O – H stretching vibrations are observed. FT-IR spectra of ADP-, KDP doped samples provide very similar features as that of pure TGSZC. More bands were located at same positions as that of pure TGSZC. From this it is observed that ADP and KDP did not change molecular structure of TGS crystal. There is a very slight shift observed in band positions compared to pure TGSZC. But doped samples provide less resolution of bands. Some bands are broadened for doped samples compared to pure TGSZC. Degeneracy is much higher for doped samples than that of pure TGSZC. This indicates the incorporation of ADP- and KDP- into the lattice of TGSZC crystal.



a



b



C

Fig. 6 Powder XRD pattern of a) TGSZC b) TGSZC+ADP c) TGSZC+KDP crystals.

3.3 FT-Raman spectral analysis

Fig. 5 shows FT-Raman spectra of pure and doped TGSZC crystals. FT-Raman spectrum of pure TGSZC matches very well with the earlier reported values of pure TGS (H.J.Byrne and E.M.Mihaylova in 2000 and R.Parimaladevi and C.Sekar). Obtained Raman bands and their assignments are tabulated in Table 3. Raman band observed at 1414cm^{-1} corresponding to symmetric stretching vibration of COO^{-} group confirms the Zwitter ion configuration of Glycine (H.J.Byrne and E.M.Mihaylova in 2000 and R.Parimaladevi and C.Sekar). Band at 1678cm^{-1} corresponding to symmetric stretching of C = O group confirms the presence of glycinium ion configuration (R.Parimaladevi and C.Sekar). In FT-Raman spectra of ADP- and KDP- doped samples some peaks were shifted to a considerable range compared to pure TGSZC. There is a change in intensity of all peaks were observed. The amount of polarisability change will determine the Raman scattering intensity. So it can be concluded that change in intensity of peaks may be due to incorporation of dopants.

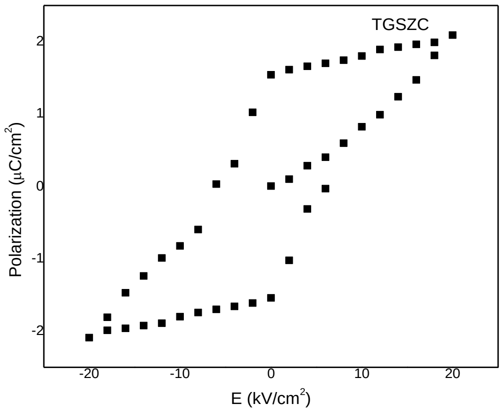


Fig. 7a

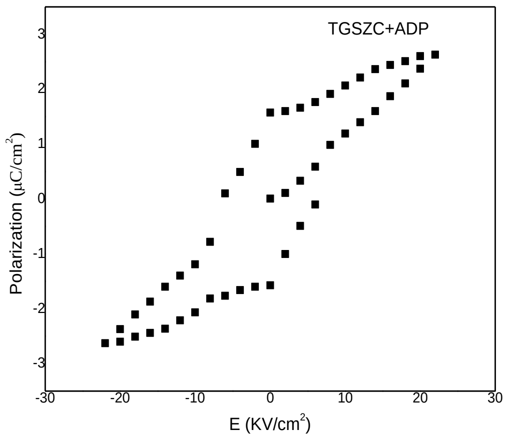


Fig. 7b

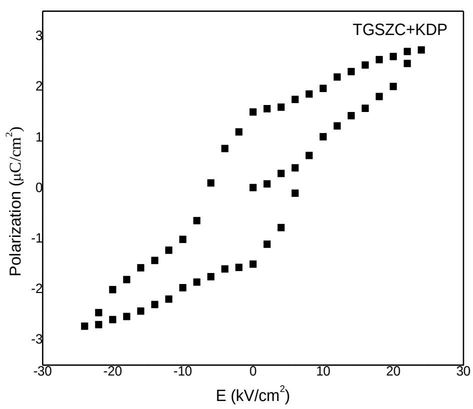


Fig. 7c

Fig. 7 Ferroelectric hysteresis loops of a) TGSZC b) TGSZC+ADP c) TGSZC+KDP crystals

3.4 Powder XRD study

Fig. 6 shows powder XRD pattern of pure and doped TGSZC crystals. All crystals belong to Monoclinic Structure. XRD pattern of grown crystals differ from each other in intensity of reflection. Doped crystals have better crystalline nature than pure TGSZC crystal. Pure TGSZC crystal has more planes of reflection than doped samples. Lattice parameter values are calculated and reported in Table 4.

There is slight changes observed in lattice parameter values for doped samples compared to pure TGSZC. Because of doping there may be some defects and strains in the doped crystals. This is the clear indication of incorporation of dopants. So pure and doped samples have different morphologies.

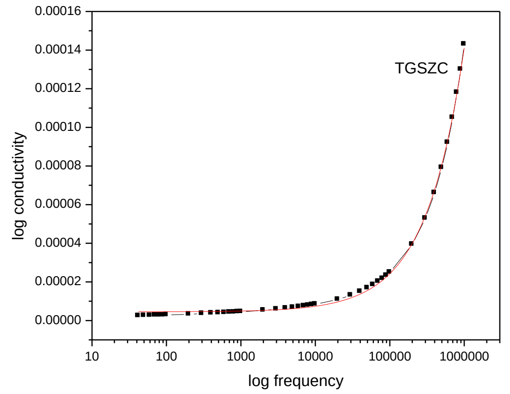


Fig. 8a

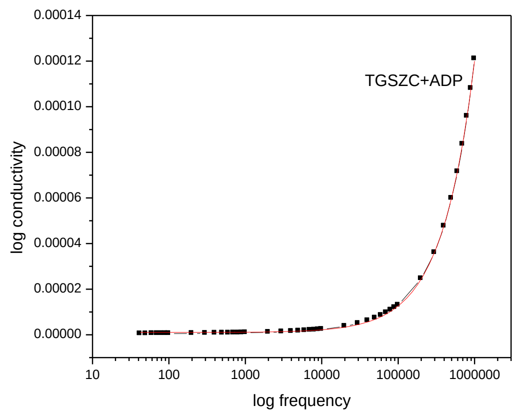


Fig. 8b

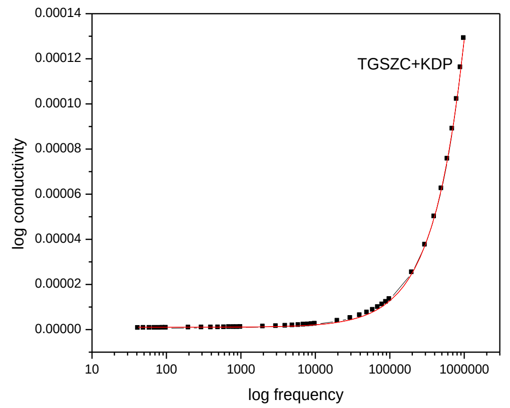


Fig. 8c

Fig.8 Frequency versus conductivity graphs of a) TGSZC b) TGSZC+ADP c) TGSZC+KDP crystals.

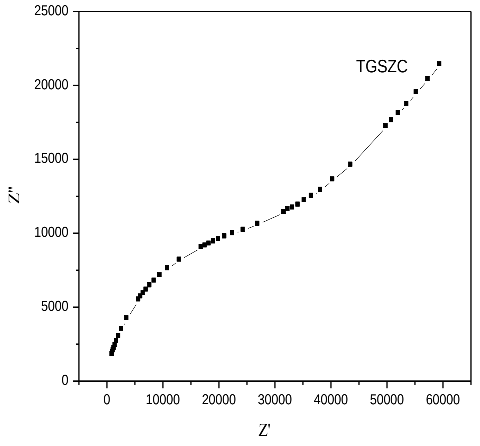


Fig. 9a

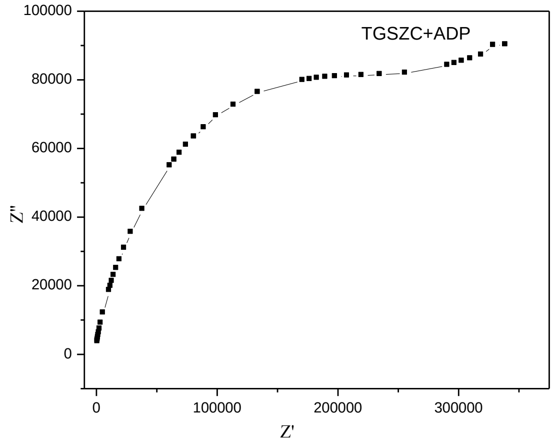


Fig. 9b

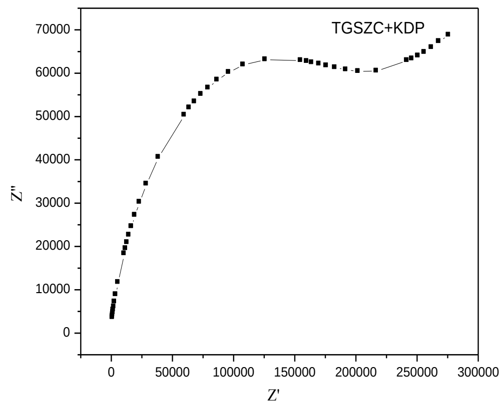


Fig. 9c

Fig. 9 Impedance graphs of a) TGSZC b) TGSZC+ADP c) TGSZC+KDP crystals

3.5 Ferroelectric hysteresis study

Homemade Sawyer- Tower circuit was constructed (C.B.Sawyer and C.H.Tower in 1930). Sample capacitors were prepared by using aluminium foils and the pure and doped TGSZC samples as dielectric in between the aluminium foils (M.Dawber et al in 2003). Spontaneous polarization values (Ps) for all samples were obtained by using the equation P = Q/A micro coulomb/cm^2.

Table 2 FT-IR Analysis of pure and doped TGSZC crystals

PURE TGSZC	TGSZC+ADP	TGSZC+KDP	ASSIGNMENT
412w – 459w (5 lines)	406w – 472w (7 lines)	405w – 459w (8 lines)	υ(PO_4), υ (SO_4)
501w	503w	501w 532w	τ(C-N)
570w	572w	574w	ν(SO_4^-)
615m 648w	615m – 648w (3 lines)	615m – 646w (3 lines)	δ(C-N), NH_3^+ oscillation
667m 675w	669m	665m 675w	υ (S-H)
866m 898m	867m 887m	866m	ν(C-C)
908w	912w	906w	υ (P-O-H), ρ(NH_3)
977S	979S	979S	ν(C-C-N),ν(SO_4^-)
1016w	-	1018w	ω(CH_2), δ(C-C), ν(C-N)
1051w	-	1051w	υ (P-O-H)
1085w	-	1085w	υ (P-O-H), υ (C=O)
1128S	-	1132S	ρ(CH_2), ν(C-C), ν(SO_4)
1309m	1311m	1309m	δ(CH_2) of Glycine ,ν(C-C)
-	1338w	-	υ (NO_2)
	1361w	-	υ (C-N)
1377m	1375m	1375m	δ(CH_2)
-	1388w	-	υ (NH_4)
-	1396w	-	υ (C=O), υ (NH_4)
-	1406w	-	δ(NH_4)
1429w	1419m	1421m 1427m	υ (COO^-), δ(CH_2)
-	1435w	1435w	δ(NH_3)
1456m – 1494w (5 lines)	1456m – 1496w (6 lines)	-	ν (NH4), ν (COO-)
1506m – 1558w (6 lines)	1506m – 1558w (7 lines)	1504m – 1556w (7 lines)	δ(NH_3)
1568m 1573w	1570m 1575w	1568m 1573w	υ (COO^-)
1616w – 1627w (3 lines)	1616w 1622w	1614w 1622w	$υ_{as}$(COO^-), δ(NH_3)
1633w -1651w (3 lines)	1635w – 1653w (3 lines)	1633w – 1651w (3 lines)	υ (O=P-OH), υ (C=C)
1660w – 1674w (3 lines)	1662w -1674w (3 lines)	1660w – 1674w (3 lines)	δ(H_2O), υ (C=C)
1683w - 1869w (16 lines)	1683w – 1992w (27 lines)	1681w – 1990w (25 lines)	υ (C=O), υ (C=NH_4)
2355m	2358m	-	Overtone and combination bands.
3500w -3558w (4 lines)	3502w – 3550w (6 lines)	3508w – 3550w (4 lines)	υ (O-H), υ (N-H)
3564wm – 3697w (15 lines)	3566w – 3687w (11 lines)	3564w -3699w (14 lines)	υ (O-H), υ (C-H), υ (C=O), δ(P-O-H)
3701w – 3959w (31 lines)	3701w – 3961w (30 lines)	3707w 3963w (26 lines)	υ (O-H) of water

$υ_s$– symmetric stretching , $υ_{as}$ – asymmetric stretching, δ – bending, ρ – rocking, ω – wagging, τ – torsional vibrations.

Table 3 FT-Raman Analysis of pure and doped TGSZC crystals

PURE TGSZC	TGSZC +ADP	TGSZC+KDP	ASSIGNMENT
74m 110m	73m 362m (4 lines)	73m – 137m (3 lines)	Lattice mode vibration of Glycine
-	-	462m	Lattice mode vibration of SO_4, δ (C-N) out of plane, ν(PO_4)
-	509m	503m – 582w (3 lines)	τ(C-N),ν(PO_4), δ(C-CO), ν (SO_4^-)
639m	666m	636m	ν(SO_4), δ(C-N) in plane, ν (S-H)
-	-	678m	ν (C-C)
870m	-	-	ν(C-C)
889w	889w	886w 890	ρ(CH_2), ρ(NH_3), ν (C-C), ν (P-O-H)
978s	978s	978s	ν(C-C-N),ν(SO_4^-)
1044w	1047w	-	ν (P-O-H), ν (SO_4)
1124w	1109w 1124w	1115w 1124w	ρ(CH_2), ν(P-O-H), ν(SO_4)
-	1214w	-	ν (PO), ν (C=O), ν(C-N-H)
1312w	1310w	1318w	δ(P-O-H)in plane, ν(C-N-H)
1414w 1441w	1441w	1413w 1441w	ν_s(COO^-), δ(CH_2), δ(NH_2), ν (NH_4)
1678w	1676w	1612w 1686w	ν (C=O), ν (O-H-O), δ(NH_2), δ(H_2O)
2063w	-	-	Overtone and combination bands
-	2116w 2648w	2487w	ν (O-H) of COOH
2726w	-	-	ν (P-O-H), ν (CH_2)
2982w	2977w 2985w	2957w – 2985w (3 lines)	ν (C-H), ν (O-H-O)
-	3164w	3018w – 3170w (3 lines)	ν (C-H), ν (NH_3^+)

υ_s – symmetric stretching, υ_{as} – asymmetric stretching, δ – bending, ρ – rocking, ω – wagging, τ – torsional vibrations.

Table 4 Lattice parameter values of grown crystals

Crystal	a (nm)	b (nm)	c (nm)	β (deg)
TGSZC	9.4396	12.7281	5.7399	110.36
TGSZC+ADP	9.4409	12.7013	5.7366	110.36
TGSZC+KDP	9.3566	12.6708	5.6532	110.36

Table 5 Ferroelectric hysteresis loop measurement values

Crystal	Spontaneous Polarization Ps (μC/cm^2)	Remnant Polarization Pr (μC/cm^2)	Coercive field value (kV/cm)
TGSZC	2.1230	1.541	6
TGSZC+ADP	2.6277	1.574	6.01
TGSZC+KDP	2.7321	1.503	6.02

Table 6 Electrical conductivity Analysis

Crystal	Electrical Conductivity Ec (Siemen/cm)	Hopping Frequency ω_p (Hz)	Charge Carrier Concentration N/cm^{-3}	Mobility μ (cm^2/Vs)
TGSZC	4.5328e-6	17340.76	0.8365e-8	33.8673e+20
TGSZC+ADP	1.0398e-6	9196.188	0.3618e-8	17.9623e+20
TGSZC+KDP	1.4308e-6	9626.76	0.3456e-8	18.8043e+20

Here Q = Charge measured on sample capacitor (coulomb). A = Area of capacitor plate (cm^2) (M.Dawber et al in 2003). Results are shown in Table 5.

3.5 Electrical Measurement

Grown crystals are subjected to electrical characterization using IMPEDENCE ANALYSER IM3570. All crystals conduct electricity linearly. Pure TGSZC crystal has higher electrical conductivity than doped crystals. Results are shown in Table 6. Fig 8 shows electrical conductivity graphs of grown crystals. Electrical conductivity graphs of pure and doped TGSZC crystals contain two regions. Frequency independent Ac conductivity region in low frequency range and frequency dependent dc conductivity region in high frequency range. Conductivity graphs obey Arhenius relation and Jonscher's power law (R.Baskaran et al (2006), C.S.Ramya et al (2006), V.D.Nithya and R.Kalaiselvan (2011) and V.D. Nithya et al (2012)). For all grown crystals dc conductivity linearly increases with increase in frequency. This indicates that electrical conductivity of these crystals is due to hopping mechanism. Electrical conductivity σ_{dc} is obtained by non linear fitting for the conductivity graphs. Then hopping frequency ω_p is obtained by using the relation $\omega_p = (\sigma_{dc}/A)^{1/n}$. Here n is frequency exponent. A is temperature dependent parameter. Chargre carrier concentration is obtained by $N = \sigma_{dc}T/\omega_p$. Mobility of charge carriers is obtained by $\mu = \sigma_{dc}/Ne$. Here e is charge of electron (V.D.Nithya et al (2012)). From electrical conductivity analysis pure TGSZC crystal has maximum dc electrical conductivity. It has higher hopping frequency, charge carrier concentration and mobility of charge carriers compared to doped samples. Fig. 9 shows Impedence graphs of pure and doped TGSZC crystals.

4. Conclusion

From UV-Vis spectra of grown crystals it is confirmed that all these crystals have excellent optical quality. This property makes these crystals useful for applications in lasers, holographic recording, optical filters and Non-linear optical applications and electro- optic applications. From FT-IR and FT-Raman spectral investigations molecular structure of pure and doped TGSZC crystals are verified. Less resolution of peaks and change in intensity of peaks for doped samples compared to pure TGSZC are due to interaction between parent and dopants. It is concluded that ADP and KDP were well incorporated into the lattice of TGSZC crystal. Ferroelectric hysteresis study reveals that for ADP- and KDP_ doped samples spontaneous polarization values were slightly increased. So doped crystals have improved ferroelectric behavior when compared with pure TGSZC. So it can be concluded that ADP- and KDP- doped TGSZC crystals are most suitable for Infrared detector applications. Zinc chloride has non linear optical property. So it can be concluded that pure and ADP-, KDP- (0.2 mol) doped TGSZC crystal may have higher S.H.G efficiency than pure TGS crystal. From electrical conductivity measurements it is observed that all crystals conduct electricity linearly and pure TGSZC crystal has higher electrical conductivity than pure doped samples.

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