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Effect of Hydrochloric Acid (HCl) on Synthesis, Spectral and Thermal Properties of Triglycine Phosphate (TGP) Single Crystals

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ABSTRACT

The effect of hydochloric acid (HCl) addition on the growth of triglycine phosphate (TGP) crystal has been studied from the aqueous solution by slow evaporation technique. Significant changes in the crystal size and morphology have been observed in all the grown samples. The structure and cell parameter values of pure and HCl doped TGP crystal are confirmed by powder X-ray diffraction analysis. The characteristics absorption bands of pure and HCl admixtured TGP crystals are confirmed by FT-Raman and FTIR spectra. Anisotropic phenomena such as therrmal, and mechanical studies have been performed. The dielectric of the crystals have been studied and the result suggests that the HCl is doped into TGP crystal and that the doping increases its dielectric parameters..

Key Words: HCl, TGP, FTIR, FT Raman, TG DTA

INTRODUCTION

The unique physical and chemical properties of crystals in the crystal symmetry, molecular structure, purity and the physiochemical environment of their formation do enhance considerably their significance in the electronic industry [1]. Especially with respect to optical devices, photonic crystals are inevitable [2,3]. The quality of optical nonlinearity would enhance the possibilities of device possibilities of photonic crystals in optical devices such as high speed optical switching for communication and even optical computing [4-10]. Hence the advancement of technologies in the above field are highly necessary. New technologies as above are focused on evolving new optical materials with better performance. The materials with a nonlinear optical (NLO) response is the most important requirement in optoelectronics. A number of NLO single crystals are identified with potential to be used in optical and electro-optical devices. Especially the solid-state laser sources are used in many such devices which further enhance the significance of nonlinear optical materials [11]. Aminoacids are interesting materials for NLO application as they contain proton donor carboxyl acid (-COO) group and the proton acceptor amino (NH_2) group in them [12]. Among the aminoacids, glycine which is found in proteins is the smallest compound used for studies [13]. Doping is a well-chosen and widely accepted technique for incorporating the required physical properties in a bulk material for technological applications [14–16]. The technique has been extensively explored to modify the properties like electrooptical (photoluminescence), conductivity and crystal growth [17].The additional impurities alter the optical and electrical properties of materials due to creation of localized states and defects created by the doping [18]. Previously glycine phosphate doped GPI [19], urea and thiourea doped GPI [20,21] have been reported. In this direction, attempts are made to dope TGP crystal with an organic complexing agent HCl(0.25, 0.50, 075 and 1.0 mole % concentrations), because the chloride ions play a partial role for NLO applicants and also the hydrochloric acid can be expected to increase dielectric constant and Tc due to its intrinsic dipole moment. Doping efforts on the growth aspects, structural perfection,

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phase transition temperature, and optical properties are studied by conducting various characterization techniques.

EXPERIMENTAL DETAILS

Material synthesis

A.R. grade chemicals of glycine and phosphoric acid selected for experimental purpose were taken in the stoichiometric ratio 3:1. Salts of estimated quantities were dissolved in double distilled water and the resultant mixture was stirred well at room temperature using a stirrer. Triglycine phosphate (TGP) salt was synthesized according to the reaction:

$$3(NH_2CH_2COOH) + H_3PO_4\ (NH_2CH_2COOH)_3.H_3PO_4.$$

For the cases HCl doped TGP solutions, the same procedure was adopted by keeping the constant amount of AC in the respective solutions. For the growth of HCl doped TGP crystals, the TGP solution was saturated by dissolving a particular amount of HCl (0.25,0.50,0.75 and 1.0mol%) in double distilled water at 30^{0}C. After saturation, the solution was filtered by means of a filter paper. The filtered solution was filtered with filter paper and the solvent was allowed to evaporate slowly at an ambient temperature in a dust free chamber. After obtaining supersaturation, the crystals were grown for a period of 10 days. Photographs of the grown crystals are shown in Figure 1.

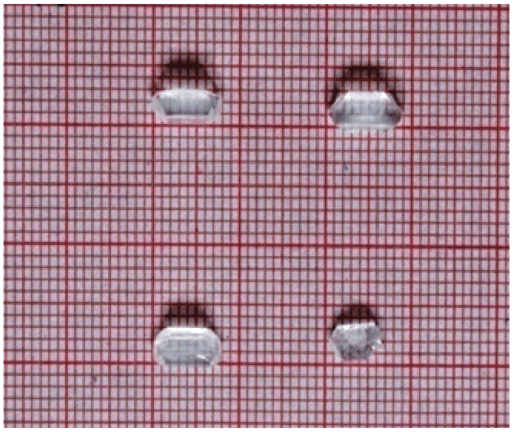

Figure 1: Photographs of the pure and HCl doped TGP grown crystals

Instrumentation

FT-IR spectra of pure and doped TGP have been recorded using Bruker IFS 66 V Spectrometer in the range 4000-100 cm^{-1}. FT Raman spectra were recorded using Bruker RFS 27: Stand FT-Raman Spectrometer with resolution of 2 cm^{-1}. UV-Vis spectra were recorded in the range of 190-1200 nm using Lambda 35 Spectrometer. Thermal analysis was carried out simultaneously employing Perkin Elmer thermogravimetric and differential analyser (Mode: PYRIS DIAMOND) in nitrogen atmosphere heated from 400 to 7300 with a heating rate of 100ºC to understand thermal behavior. Dielectric studies of the grown crystals were carried out to an accuracy of ±2ºC using an LCRZ meter with five different frequencies, viz. 100 Hz,1 KHz, 10 KHz, 100 KHz and 1 MHz at various temperatures ranging from 30ºC to 150ºC.

RESULTS AND DISCUSSION

Powder XRD Analysis

Single crystal XRD data of the pure TGP crystal suggests that the crystal belongs to monoclinic structure. In order to confirm the material of the grown crystal, powder XRD data was collected from the pure and hydrochloric added TGP crystals.

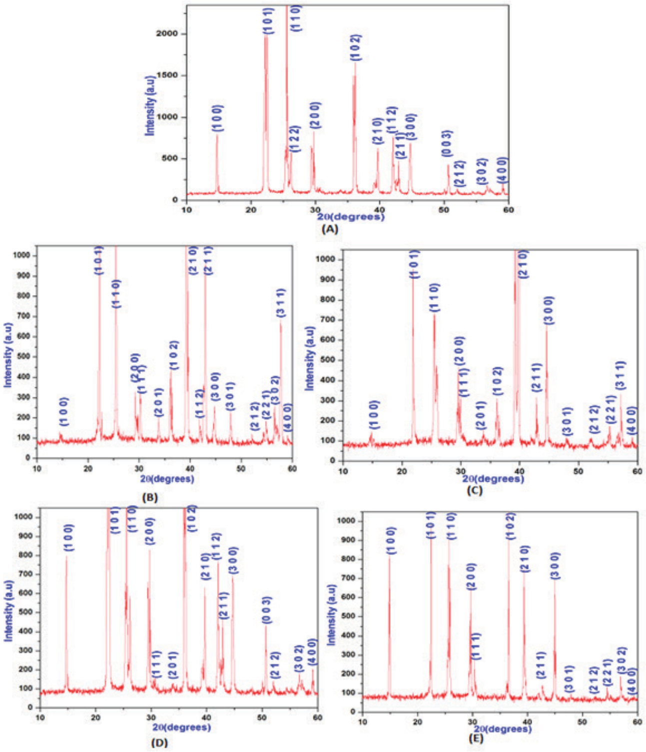

Figure 2: Powder XRD patterns for the grown (A) Pure TGP (B) 0.25 mol % HCl doped TGP (C) 0.50 mol % HCl doped TGP (D) 0.75 mol % HCl doped TGP (E) 1.0 mol % HCl doped TGP crystals

The high crystalline nature of the grown crystals is revealed by the prominent and well resolved Bragg's peak at specific 2θ angle .Using observed 2θ(Bragg angle) and d (interplanar spacing) all the reflections were indexed (JCPDS file). Powder diffractogram and (h k l) values of the pure and HCl admixture TGP are shown in Fig 2. Comparing PXRD patterns of doped crystals with those of pure TGP single crystal, small changes in'd' - spacing values were observed, which may be attributed to the presence of dopants in TGP crystal. All the grown crystals a ≠ b ≠ c ensure that all the grown crystals is of monoclinic structure [22].The data lattice parameters and the cell volume were calculated and are given in Table 1. Analysis of the PXRD spectra confirmed the excess HCl only acted as the additive rather than as dopant.

Table 1: Unit Cell parameters of pure and hydrochloric acid admixtured TGP crystals

Sl No	Sample	Cell parameters	Volume
1	Pure TGP	a =6.7985 Å(2) b= 11.9892Å(5) c= 8.1913Å(7)	667.6625 (Å)^3
2	0.25 mole % HCl+TGP	a = 7.0299Å(3) b= 11.2286Å(2) c= 8.6442Å(6)	682.3375 (Å)^3
3	0.50 mole % HCl+TGP	a = 7.0580 Å(7) b= 11.7385Å(6) c=8.1953 Å(4)	596.1389 (Å)^3
4	0.75 mole % HCl+TGP	a =7.3091 Å(8) b= 11.4983 Å(6) c= 8.4913Å(8)	682.3375 (Å)^3
5	1.0 mole % HCl+TGP	a = 7.1427Å(4) b= 12.1662Å(4) c= 8.9789 Å(2)	665.0472 (Å)^3

FT-IR and FT-Raman Analyses

Figure 3(a) and (b) show the FT-IR and FT Raman spectra of pure and HCl doped TGP crystals as it were recorded in the region 400-4000 cm^{-1} and the vibrational assignments were given in Table 2. Asymmetric and the symmetric stretching mode of NH_2 appear 3380-3350 cm^{-1}and 3310-3280 cm^{-1}respectively [23]. Asymmetrics tretching mode of $NH_2$is observed as a strong broad band in IR at3110 cm^{-1}and the symmetric stretching mode is observed in Raman at 2962cm^{-1}. The band observed at 2962.97 cm^{-1} and 2890.02 cm^{-1} are assignable to CH_2 stretching mode. P-O stretching vibrations are expected in the region 1040-910cm^{-1} [24] which is observed in IR at ~1042 and 926 cm^{-1}with the counterpart in Raman at ~900 cm^{-1}.Generally H-Cl stretching mode is observed at 685-680 cm^{-1} which is observed in IR at ~683 cm^{-1}. Its absence in the pure TGP spectrum and its presence in the doped TGP spectra clearly indicate the presence of Cl^- in the lattice of TGP crystal. C=O stretching vibrations in saturated aliphatic aldehydes, ketones and acids have frequencies in range 1740–1700 cm^{-1}. In amides the frequency is lowered to 1690 cm^{-1} [25] which is due to existence of resonance structures.C=O stretching band is observed at 1590 cm^{-1}. The deformation vibration of the carboxylate ion is observed at 682.95 cm^{-1}. C=O and NH_2 stretching vibrations are shifted and strongly evidences of intra-molecular interactions.CH_2stretching vibration is observed at 2890, 2792 and 2605cm^{-1}.

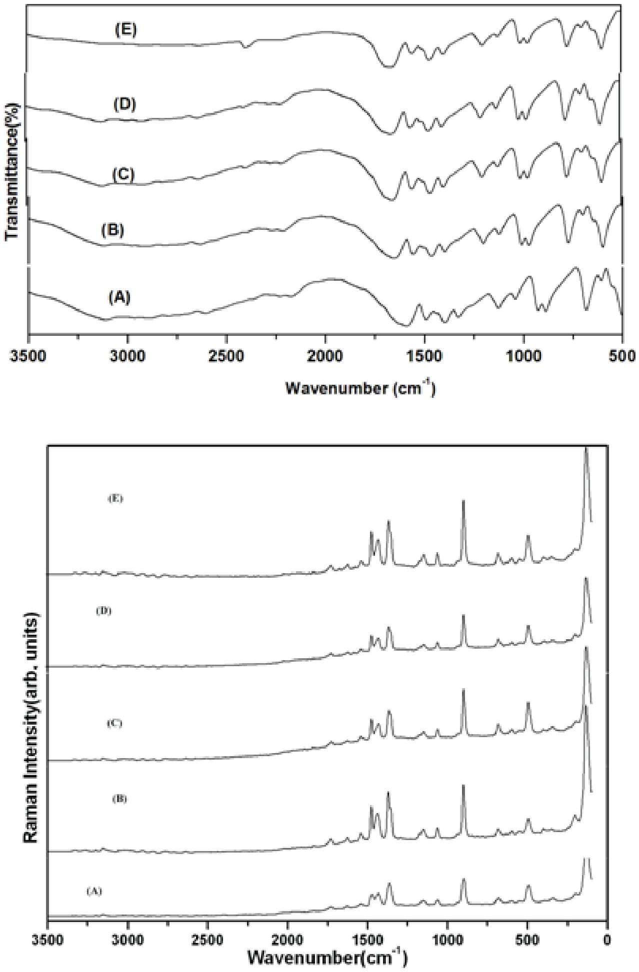

Figure 3: FT-IR and FT-Raman Spectra for the grown (A) Pure TGP (B) 0.25 mol % HCl doped TGP (C) 0.50 mol % HCl doped TGP (D) 0.75 mol % HCl doped TGP (E) 1.0 mol % HCl doped TGP crystals respectively

Thermal Analysis

Thermogravimetry (TG) and differential thermal analysis (DTA) of pure and HCl doped TGP were carried out at room temperature to 730ºC and the thermograms are depicted in Fig.4. In pure TGP, up to 200ºC there is no weight loss which reveals that the compound is devoid of physically adsorbed water and water of crystallization [26].Slight variations appear in the TGA traces of HCl doped TGP crystals with various concentrations 0.25, 0.50, 0.75 and 1.0 mole % that are 203, 185, 206 and 195 respectively.

Table 2: Vibrational assignments of pure and HCl doped TGP crystals

Pure TGP (cm^{-1})		TGP Doped with HCl(cm^{-1})								Assignments
		0.25mole%		0.50mole%		0.75mole%		1.0mole%		
3110	3156	3106	3153	3107	3155	3105	3147		3147	$\nu_{as}NH_2$
2962		2962		2962		2969				$\nu_{ss}NH_2$
2890	2920	2890	2905	2910	2908	2889	2912	2859	2912	νCH_2
2792		2790		2795		2790		2738		νCH_2
2605		2604		2606		2604		2603		νCH_2
	1730		1730		1726		1726		1730	νC=O
	1628		1626		1630		1623		1627	νC=O
1590	1542	1591	1540	1595	1542	1594	1540	1600	1540	νC=O
1490	1472	1491	1476	1491	1476	1491	1476	1491	1476	βNH_2
	1434		1438		1432		1432		1432	βNH_2
1395	1362	1395	1372	1396	1366	1395	1368	1400	1368	$\nu_{ss}COO^-$
1326		1327		1326		1327		1327		νP=O
1125	1154	1125	1150	1124	1148	1124	1152	1123	1148	νP=O
1041	1062	1041	1062	1043	1060	1041	1062	1042	1062	νP- O
926		926		926		927		926		COO deformation
887	898	888	902	888	900	888	900	888	900	υ (C-C)
	682	683	686	683	684	683	684	682	686	νHCl
607	604	607	601	607	600	607	600	608	604	δ(C-N)
501		502		502		502		502		(COO^-)
	400		403		400		399		399	(C-N) out of plane
	344		363		348		352		350	τ(C-C)

ν-stretching; ν_{as-}asymmetric stretching; ν_{ss-}symmetric stretching; β-Bending; δ-out of plane bending ; τ- torsion

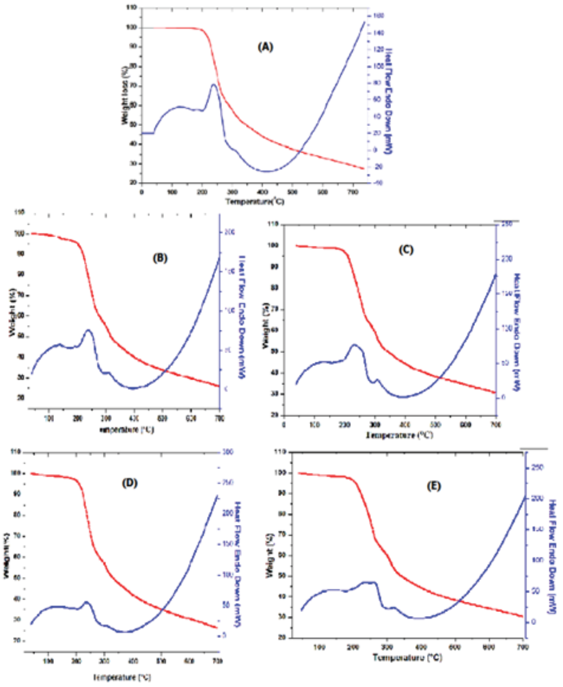

Figure 4: TG – DTA curve of the grown (A) Pure TGP (B) 0.25 mol % HCl doped TGP (C) 0.50 mol % HCl doped TGP (D) 0.75 mol % HCl doped TGP (E) 1.0 mol % HCl doped TGP crystals.

The decomposition of the compound takes place in single stage. Between 243ºC and 730ºC the weight loss of 71% is observed. This weight loss is due to the loss of glycine fragments in the compound. This weight loss decreases as the concentration increases (242, 241, 239and 233ºC).The decomposition pattern is explained based on the formulated pattern of the compound which accounts for 70.094 to -54 % weight loss. The variation of experimental and the formulated weight losses are insignificant. At 730ºC, almost 29 % of the compound remains as residue. An exothermic peak observed in DTA at 238ºC complement to HCl admixtured TGP are due to the decomposition of the compound. Pure TGP crystal showed a major weight loss (~49 wt.%) in the temperature range between 218 and 268ºC. This can be attributed to the decomposition of glycine into CO_2 and HCl. DTA curve revealed a sharp peak at 233ºC corresponding to the decomposition of glycine. Further increase in temperature resulted in the removal of HCl in the form of H_2O with a total weight loss of 24 wt.%. Thus DTA curve of TGP crystal also showed to be due to combustion of glycine and removal of carbon. Melting point of Pure and HCl admixtured TGP crystals are given in Table 3.

Table 3: Melting Point of pure and HCl doped TGP crystals

Crystals	Melting Point
Pure TGP	412
TGP+0.25 mole % HCl	398
TGP+0.50 mole % HCl	399
TGP+0.75 mole % HCl	378
TGP+1.0 mole % HCl	387

AC Electrical Conductivity Studies

The capacitances for various frequencies in the range of 100Hz to 1MHz at different temperatures of the samples were measured. The variation of dielectric constant(ε_r) with temperature at various frequencies of pure and HCl admixtured TGP crystals with various concentrations (0.25, 0.50, 0.75, 1.0 mole %) were shown in Fig. 5.The dielectric constant is small at low temperature, which increases with temperature for pure and HCl admixtured TGP crystals, reaching maximum at the Curie point T_c.(328K).The rapid increase may be due to the space charge polarization of thermally generated carriers [27]. Above T_c.(328K), the dielectric constant decreases, following the Curie–Weiss law. It shows that all the grown crystals (pure and doped TGP) behave as para electric before 328K and becomes ferroelectric above 328K, at varying frequencies. Thus all grown crystals may exhibit ferroelectric nature at higher temperatures. It is noticed that there is very small change of Curie temperature when TGP crystal is doped with HCl at various concentrations. HCl being a dipolar impurity, creates a high dipole moment in the TGP lattice, thereby increasing the dielectric constant. Moreover the observed enhancement in the dielectric constant at low frequency could be attributed to the multi domain state of the HCl doped sample. The magnitude of dielectric constant depends on the degree of polarization charge displacement in the crystals. The increase in dielectric constant for HCl admixtured TGP crystal may be due to frittering of domains in the space charge polarization of thermally generated carriers [28]. Also the increase in dielectric constant for HCl doped TGP crystals may be due to frittering of domains due to the incorporation of impurities into TGP crystal lattice [29]. The peak value of dielectric constant was found to decrease with frequency. Very small significant shift in the temperature of dielectric maxima with different frequencies was found, which shows the absence of any relaxation behavior. According to Miller's rule, the low value of dielectric constant enhances SHG coefficient [30]. The variation of dielectric loss(tan δ) with temperature at various frequencies of pure and HCl doped TGP crystals with various concentrations (0.25, 0.50, 0.75, 1.0 mole %) were shown in Fig. 6. At higher frequencies due to the low value of dielectric constant and dielectric loss, its optical quality is enhanced with lesser defects which are important parameters for making it useful for various NLO applications [31]. This low value of dielectric loss indicates that crystal has minimum defects [32].

A plot of ln σ_{ac} versus 1000/T gives -Ea/k as the slope and ln σ_{ac} as the intercept. Activation energies at the ferroelectric phase (above Tc) of the grown crystals are estimated using the slopes of the line plots, [E= -(slope)k x1000] and are found to be 0.5255eV ,0.2039eV , 0.2454eV, 0.2454eV, and 0.5851eV respectively for pure and HCl doped TGP (0.25,0.50, 0.75 and 1.0 mol %) crystals. A similar range of activation energy values have been reported which infer that pure and Hydrochloric acid added crystals will behave at high temperatures as a super-ionic conductor [33]. The lower activation energies estimated from electrical conductivity studies suggest that the material contains less number of charge carriers for conduction process and the dielectric behavior is very well understood.

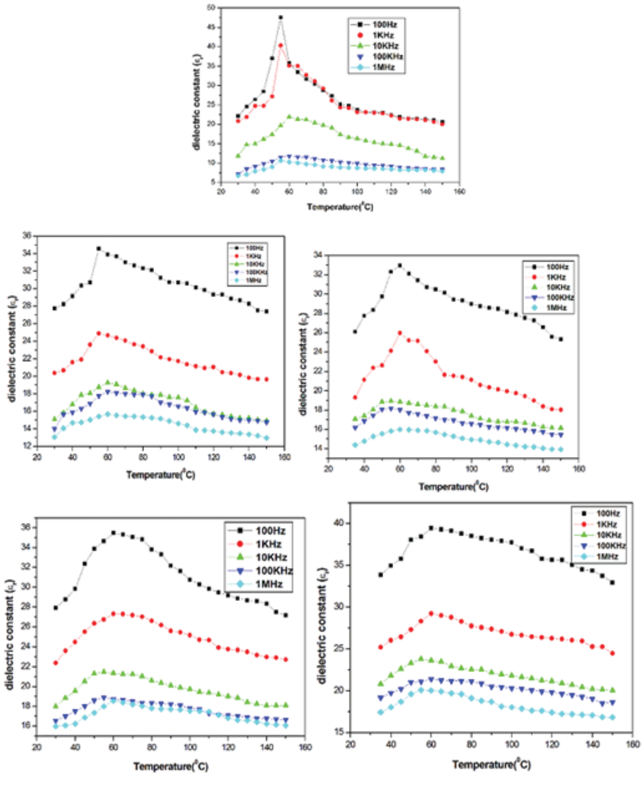

Figure 5: Variation of Dielectric constant (ε_r) with Temperature for the Pure and HCl doped TGP crystals

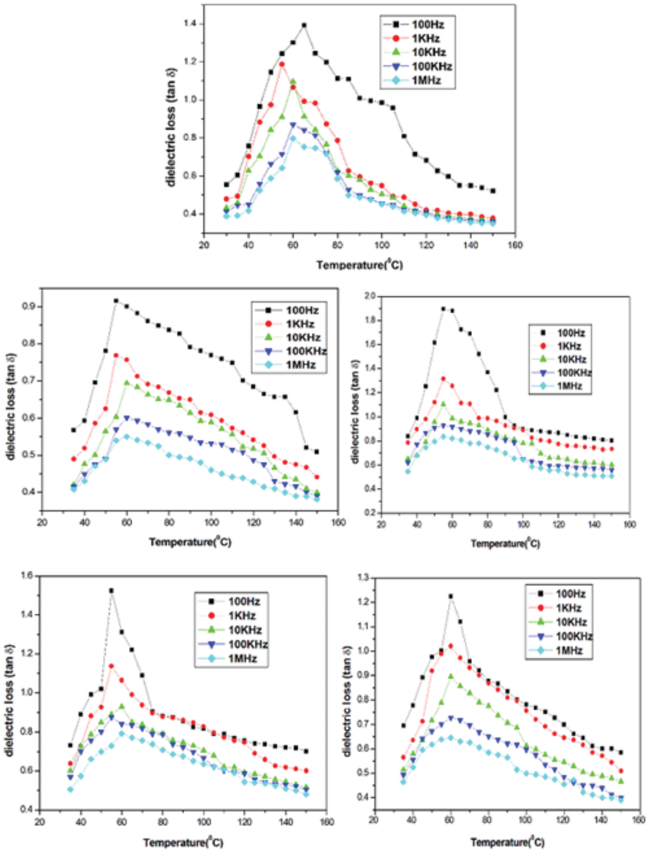

Figure 6: Variation of Dielectric Loss(tanδ) with Temperature for the Pure and HCl doped TGP crystals

CONCLUSION

Good optical quality crystals of pure and HCl (0.25, 0.50, 0.75 and 1.0 mole %) doped TGP crystals were grown successfully from aqueous solution by slow evaporation technique. The spectral investigations by IR and Raman spectroscopy strongly suggested that the Zwitter and glycinium ions were present in both pure and HCl admixtured TGP crystals. C=O and NH_2 stretching vibrations are slightly shifted and there are strong evidences of intra-molecular interactions. Pure and HCl doped TGP crystals are useful as a good non-linear material and for optoelectronics applications due to low cut off wavelength and are transparent to the entire visible region, which shows the wide window for nonlinear applications. Observed low dielectric constant and low dielectric loss suggests that the grown crystals are suitable for NLO applications in accordance with Miller's rule.

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