International Journal of Chemical Sciences and Applications
ISSN 0976-2590, Online ISSN 2278 – 6015
Vol 4, Issue 1, 2013, pp 29-38
http://www.bipublication.com

THEORY OF IRON DOPED DEUTERATED TRIGLYCINE SULPHATE DOPED TRIGLYCINE SULPHATE (Fe-DTGS) CRYSTAL

Ashish Nautiyal and T C Upadhyay

Physics Department, H.N.B.Garhwal University, (A Central University),
Srinagar Garhwal, Uttarakhand, India-246174
Email: andehradun@yahoo.com, ashishnautiyalphysics@gmail.com

[Received-07/12/2012, Accepted-10/01/2013]

ABSTRACT

A theoretical approach to explain singular thermodynamic function in order to predict a phase transition in hydrogen bonded ferroelectric Iron doped deuterated triglycine sulphate (Fe-DTGS) crystal and energy propagation in terms of correlation function of inter and intra chain interaction harmonic and anharmonic. This study is extended to third, fourth and higher order phonon anharmonic interactions of two sub-lattice form of the crystal vibrations. Proton tunnelling theory and pseudo vibration model is supported by the blinc and chaudhuri's theory about phase transition in hydrogen bonded ferroelectric crystals. Our dynamic approach is very near to cocharan theory. To define spectral density function, we have implemented time dependent thermal Green's function. Heavy atom displacements are almost perpendicular to spontaneous polarization which is solved by fourth particle cluster theory. Our theory defines the pseudospin character of proton particle in molecular field of a monoclinic system. We have calculated soft mode frequency, lattice frequency shift and width, dielectric constant, loss tangent, quality factor, acoustic attenuation, electric conductivity, relaxation time, smooth function and ratio of figure of merits M_2/M_1, M_3/M_2, M_3/M_1 characteristics of the Iron doped deuterated triglycine sulphate (Fe-DTGS) crystal. We have considered external electric field effects on ferroelectric properties of the crystal also. Our calculated results have a good agreement with experimental data.

Keywords: Figure of merits, pseudo-vibrations, correction functions etc.

[I] INTRODUCTION

Triglycine sulphate ($NH_2CH_2(CH_3COOH)_3.H_2SO_4$) is a pyroelectric type ferroelectric crystal which is a very famous material in infrared detection and computing technologies etc. has discovered by Matthias et al in 1956 [1]. If its hydrogen atoms (H) is replaced by hydrogen isotopes deuterium (D) then it change in to deuterated triglycine sulphate (DTGS) crystal ($ND_2CD_2(CD_3CO\,OD)_3.D_2SO_4$). Deuterated triglycine sulphate crystal is monoclinic in both phases. DTGS crystal transform ferorlectric phase P_m to paraelectric phase $P_{2/m}$ at 333.86 K. Lattice dimensions of deuterated triglycine sulphate (DTGS) crystal are; a=9.462 Å, b= 12.706 Å, c= 5.746 Å, V= 690.81 $Å^3$ and β= 110.35^0 [2].

Strukov and colleagues have [3–7] examined spontaneous polarization, thermodynamic, calorific relation and electro-conductive

properties of triglycine family crystal (TGS, TGSe). As we see below, that the important consideration is the dependency of entropy S (E, T) upon temperature and applied electric field. In this respect it may be useful to study the ferroelectric known to exhibit maximum entropy change at T_c: ammonium sulphate [$(NH_4)_2SO_4$], for which both ammonium ions and sulphate ions disorder at Tc, given 17.6 J $(mol \cdot K)^{-1}$, approximately an order of magnitude larger than in most ferroelectrics [8, 9]. A heat cycle consisting of four steps (or legs), of which two are usually isothermal (or sometimes at constant field) and two are adiabatic [10] published a nice study of this material in 2008, the material's ionic conduction is too high to permit the material to withstand a large field, so commercial devices based on this material are very unlikely. Some chemistry research on the materials science of ammonium sulphate should be carried out to reduce its ionic conductivity, perhaps by admixtures.

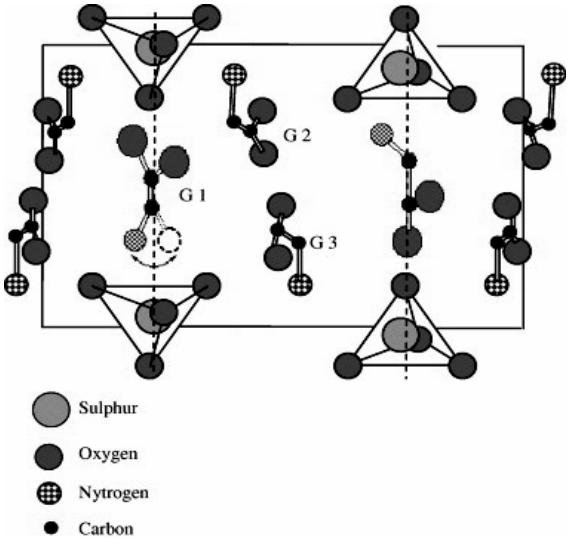

Fig. 1. Glycine ions (I, II, III) in deuterated triglycine sulphate (DTGS) crystal.

The unit cell of triglycine sulphate (TGS) crystal consists of three glycine groups, namely glycine-I (GI), glycine-II (GII), glycine-III (GIII) and a sulphate ion in an asymmetric unit. The structures of its ferroelectric and paraelectric phases were determined using neutron as well as X-ray diffraction [11, 12] with the space groups being P21 and P21/m respectively. The two glycine groups GII and GIII are quasi-planar. They are arranged nearly perpendicular to the polar b-axis and are connected together by a strong hydrogen bond GIII-HO_3. The hydrogen atom in this H-bond has two equivalent positions of HO ions, which are closer to GIII and GII re- spectively. The GI lies close to the ac plane at 0.25b with its two carbon atoms and two oxygen atoms lying almost in the ac plane at 0.25b whereas the nitrogen is displaced significantly from the plane. The NH+3 group of GI has two equivalent positions, one on the left (L) and the other on the right (R) of the above-mentioned ac plane. For temperatures higher than transition temperature (Tc), the hydrogen in the H-bond GIII-H (GII and the NH+3 group of GI are disordered between their equivalent sites) making the ac plane (at 0.25b (M)) a statistical mirror plane [13]. A comparison of the average amplitudes of motion of the heavy atoms near Tc shows Phase transition in hydrogen bonded triglycine family that the nitrogen atom of

GI has a maximum amplitude in the b direction, which points to a possible driving role for the nitrogen double-well instability in the mechanism of the ferroelectric transition. Also, the insignicant effect of deuteration on the dielectric properties of TGS (e.g. Tc is increased by only about 3% in TGS as compared to 80% increase in KDP) suggests that the role of hydrogen tunnelling in the H-bond GIII-H. GII may be less dominant as compared to the dynamics of NH+3 group of GI. The structure of the two ferroelectric domains of TGS are a mirror image of each other [13]. When the polarization of a TGS unit cell reverses, the NH+3 group of GI moves from one of its equivalent positions, say L to the other R and the hydrogen in the H-bond GIII-H (GII moves along the bond from one of its equivalent positions HO to the other HO ions).

The major disadvantage of using ferroelectric crystals as pyroelectrics is the possibility of a

single domain crystal becoming multi-domain (i.e. depoling of the crystals) during the application. One of the effective ways of preventing depol- ing in TGS is by doping it with alanine (NH_2CHCH_3COOH), which is a molecule similar to glycine (NH_2CH_2COOH) with the only difference being the presence of CH_3 group in alanine in place of one of the two hydrogens of glycine. It is found that the addition of alanine to TGS results in a net internal bias field and the crystals containing alanine retain their self-bias even after prolonged heating above the Curie temperature as well as after the application of large reverse bias electric fields.

Pure TGS crystals possess many disadvantages such as (i) high ferroelectric domain mobility at room temperature, (ii) polarization reversal by electrical mechanical and thermal means, (iii) microbial contamination during the growth and (iv) low Curie Krishnakumar, Rajaboopathi and Nagalakshmi temperature. In order to overcome this unfavourable for practical application features variety of dopants such as amino acids, organic and inorganic compounds or deuterated forms have been introduced [14-17]. Due to the competent nonlinear optical efficiency of amino acids and its complexes many researchers have reported with inorganic salts and that has proved as a good candidate for nonlinear optical applications [18-20]. Various metallic ion dopants such as Mn2+, Ni^{2+}, Fe^{3+}, Cr^{3+}, Cu^{2+} etc., added to modify the optical properties of TGS crystals [21-24]. Rare earth metal ions like La, Ce and Nd were used to modify the morphology and the coercive field values of TGS crystals. Incorporation of inorganic additives into an organic material can alter the various physical properties in order to achieve better performance in opto-electronic devices**.** The presence of metallic species in the organic compounds generally raises the hardness of the compounds considerably [25]. Recently alkali metal chloride doped TGS have been reported as high dielectric constant and low hardness values [26]. Infrared application of DTGS crystal has been proposed by many authors [27].

In the case of deuterated analogs of TGS, it is not possible to completely replace the hydrogen with deuterium. There are seventeen hydrogen in each TGS molecule. Among the seventeen, eleven are active (64.7%) except the six which are in contact with carbon atom .These eleven active H can be substituted with deuterium by recrystallization [28]. DTGS and doped crystals grown during this study have shown to possess superior properties such as materials figures of merit, growth yield and ease of handling over pure DTGS crystals, and are, therefore, very useful and attractive for IR sensing device applications. Pure and doped DTGS crystals, respectively. It can be inferred that presence of dopants in the process of crystal growth results in changes in growth rates along [001] and [010] directions and the growth yield. The growth is anisotropic in nature. It is relatively higher along [010] directions compared to [001] direction; thereby, we observed smaller {010} faces as compared with {001} faces in both pure and doped DTGS crystals. [29]

Pyroelectric detecting materials possess a number of characteristics which are of significance when considering their use in a given application. They can be used over a large spectral bandwidth, the only requirement being that the energy be absorbed. They can be used over a wide range of temperatures. They have low power requirements and can operate for long period on battery power, and last, but not least, they are generally low-cost devices. Some of the devices built with crystals of TGS family are (i) Intruder alarms (ii) Fire alarms (iii) Pollution monitoring and gas analysis (iv) Radio meters (v) Laser detectors (vi) Pyroelectric thermal imaging (vii) Pyroelectric vidicon and (viii) Pyroelectric arrays. DTGS is a successful high sensitive detector type used as infrared spectrometers which is used to take measurements in the mid-infrared (mid IR) range.

For better quality results in ferroelectric, dielectric, pyroelectric properties of the crystal,

we have chosen impure Iron doped deuterated triglycine sulphate (Fe-DTGS) crystal. Impurity level of iron in the crystal is considered 0.25% molecular weight. This impurity concentration does not make any structural changes in the crystal body.

[II] THEORY

To solved Iron doped deuterated triglycine sulphate crystal we have applied two sub lattice pseudospin lattice coupled mode model [30] and Ising spin model [31] of ferroelectrics. In application of these models the major problem was to solve inhomogeneous behaviour of eigen values and eigen functions of the crystal which is solved by Green's function theory [32].

Hamiltonian of Iron doped deuterated triglycine sulphate crystal (Fe-DTGS),

$$H=-2\Omega\sum_i\left(S_{1i}^x+S_{2i}^x\right)-\sum_{ij}J_{ij}\left[\left(S_{1i}^zS_{2i}^z\right)+\left(S_{2i}^zS_{2i}^z\right)\right]$$

$$-\sum_{ij}K_{ij}\left(S_{1i}^zS_{2i}^z\right)-2\mu E\sum_i(S_{1i}^z+S_{2i}^z)+\frac{1}{4}\sum_k\omega_k\left(A_kA_k^++B_kB_k^+\right)$$

$$-\sum_{ik}V_{ik}S_{1i}^zA_k-\sum_{ik}V_{ik}S_{2i}^zA_k^+.....$$

$$+\sum_{k_1k_2k_3}V^{(3)}\left(k_1,k_2,k_3\right)A_{k_1}A_{k_2}A_{k_3}$$

$$+\sum_{k_1k_2k_3k_4}V^{(4)}\left(k_1,k_2,k_3,k_4\right)A_{k_1}A_{k_2}A_{k_3}A_{k_4}.....$$

$$+\sum V(Iron-Interactions)$$

…(1)

Where In equation (1) above Ω is proton tunneling frequency, S^z and S^x are components of pseudospin variable J_{ij} is interaction between same lattices and K_{ij} is interaction between different lattices. μ is dipole moment of O-H--O bond, E is external electric field V is spin lattice interaction and A_k and B_k are position and momentum operators ω_k is harmonic phonon frequency $V^{(3)}$ and $V^{(4)}$ are third and fourth order atomic force constant

Equation have been solved by the Green's function theory

$$G_{ij}(t-t')=\left\langle\left\langle S_{1i}^z(t);S_{1j}^z(t')\right\rangle\right\rangle$$

$$=-i\theta(t-t')\left\langle\left[S_{1i}^z(t);S_{1j}^z(t')\right]\right\rangle,\qquad\ldots(2)$$

in which θ(t- t') step function is zero for $t<t'$ and unity for $t>t'$. The angular bracket <-----> denotes ensemble average over a grand canonical ensemble.

Spontaneous polarization in Fe-DTGS crystal is

$P_s=2N_\mu\langle s^z\rangle$ …(3)

In two dimensional form of pseudospin in z-directional sum is not zero before T_C (Curie temperature).

$S_1^Z+S_1^Z\neq0$;

And $S_1^Z\neq S_1^Z$; For $T<T_C$,

But after curie temperature total spontaneous polarization become zero.

$S_1^Z+S_1^Z=0$; For $T>T_C$,

Specially for Fe-DTGS crystal (ferroelectric) both spin become zero.

$S_1^Z=S_1^Z=0$; For Fe-DTGS (ferroelectric crystal) crystal at phase transition, while S_1^Z; $S_1^Z>0$; but $P_S\rightarrow0$ not exactly zero.(for second order phase transition)

$$\langle S^x\rangle=\frac{\Omega}{\tilde{\Omega}}\tanh\left(\frac{\beta\tilde{\Omega}}{2}\right)$$

$$\langle S^y\rangle=0$$

$$\langle S^z\rangle=\frac{(J_0\langle S^Z\rangle+J_0'\langle S^Z\rangle^3)}{2\tilde{\Omega}}\tanh\left(\frac{\beta\tilde{\Omega}}{2}\right)\qquad\ldots(4)$$

These are obtained as following

Spin shift is

$$\Delta_s(\omega)=\frac{a^4}{2\Omega\left(\omega^2-\tilde{\Omega}^2\right)}+\frac{b^2c^2}{4\Omega\tilde{\Omega}}$$

$$+\frac{V_{ik}^2N_ka^2}{2\Omega\left(\omega^2-\tilde{\Omega}^2\right)}+\frac{4\mu^2E^2a^2}{2\Omega\left(\omega^2-\tilde{\Omega}^2\right)}$$

and higher order spin shift is

$$\Delta_{s-p}(\omega)=\frac{2V_{ik}^2\langle S_{1i}^x\rangle\omega_k\delta_{kk^i}\left(\omega^2-\tilde{\tilde{\omega}}_k^2\right)}{\left[\left(\omega^2-\tilde{\tilde{\Omega}}_k^2\right)^2+4\omega_k^2\Gamma_k^2(\omega)\right]}\qquad\ldots(5)$$

Spin width is

$$\Gamma\ (\omega) = \frac{\pi a^4}{4\Omega\tilde{\Omega}}\left[\delta\left(\omega - \tilde{\Omega}\right) - \delta\left(\omega + \tilde{\Omega}\right)\right]$$

$$+ \frac{b^2c^2}{4\Omega\tilde{\Omega}}\left[\delta\left(\omega - \tilde{\Omega}\right) - \left(\omega + \tilde{\Omega}\right)\right]$$

$$+ \frac{V_{ik}^2 N_k a^2}{4\Omega\tilde{\Omega}}\left[\delta\left(\omega - \tilde{\Omega}\right) - \delta\left(\omega + \tilde{\Omega}\right)\right]$$

$$+ \frac{2\pi\mu^2 E^2 a^2}{4\Omega\tilde{\Omega}}\left[\delta\left(\omega - \tilde{\Omega}\right) - \delta\left(\omega + \tilde{\Omega}\right)\right]$$

and higher order spin phonon width is

$$\Gamma_{s-p}(\omega) = \frac{4V_{ik}^2\langle S_{1i}^x\rangle\omega_k\left(\omega^2 - \tilde{\tilde{\omega}}_k^2\right)}{\left[\left(\omega^2 - \tilde{\tilde{\omega}}_k^2\right)^2 + 4\omega_k^2\Gamma_k^2(\omega)\right]} \quad \ldots(6)$$

2.1. Dielectric constant and loss tangent

The response of a dielectric crystal to the external electric field is expressed dielectric susceptibility χ given as

$$\chi(\omega) = -\lim_{X\to 0} 2\pi N\mu^2 G_{ij}(\omega + iX) \quad \ldots(7)$$

The $\chi(\omega)$ is related to dielectric constant as

$$\in = 1 + 4\pi\chi \quad \ldots(8)$$

With the help of Eq.(7) and (8) one obtain expression for dielectric constant as

$$\in(\omega) = \left(-8\pi N\mu^2\right)\frac{\left\langle S_1^x\right\rangle\Omega}{\left[\left(\omega^2 - \hat{\Omega}^2\right)^2 + 4\Omega^2\Gamma^2\right]} \quad \ldots(9)$$

$\in(\omega) >> 1$ in the ferroelectric crystal. The power lost in dielectric when exposed to electromagnetic field is conveniently shown as dielectric tangent loss which is expressed as

$$\tan\delta = \frac{\in''}{\in'} \quad \ldots(10)$$

By using Eq. (9) and (10) we obtains expression for loss tangent as

$$\tan\delta = -\frac{2\Omega\Gamma(\omega)}{\left(\omega^2 - \hat{\Omega}^2\right)} \quad \ldots(11)$$

2.2. Quality factor

Q–Factor=1/tanδ …(12)

Where , tanδ=tangent loss

2.3. Acoustic attenuation

The acoustic attenuation is given as

$$\alpha = \frac{\Gamma(\omega)}{\nu} \quad \ldots(13)$$

Where, $\Gamma(\omega)$ is width and ν is sound velocity.

2.4. Ratio of Figure of Merits

We know that dielectric permittivity can be written as

$$\varepsilon = \varepsilon' \pm i\varepsilon'' \quad \ldots(14)$$

where, ε' =real part of permittivity

ε'' =imaginary part of permittivity

and magnitude of this complex number will be

$$\varepsilon = \sqrt{(\varepsilon'^2 + \varepsilon''^2)} \quad \ldots(15)$$

and dielectric loss

$$\tan\delta = \frac{\in''}{\in'} \quad \ldots(16)$$

Solve eq.(15) and eq.(16)

We have

$$\varepsilon' = \sqrt{\left(\frac{\varepsilon^2}{1 + \tan^2\delta}\right)}$$

and,

$$\varepsilon'' = \sqrt{\frac{\varepsilon^2\tan^2\delta}{1 + \tan^2\delta}} \quad \ldots(17)$$

in Infra-Red detection we can write the figure of merit can be written as

$$M_1 = \frac{\rho}{\varepsilon'}$$

High current responsivity

$$M_2 = \frac{\rho}{\sqrt{\varepsilon''}}$$

And vidicons application

$$M_3 = \frac{\rho}{\sqrt{\varepsilon'}}$$

Then relative figure of merits will be

$$\frac{M_2}{M_1} = \sqrt{\varepsilon''}$$

$$\frac{M_3}{M_2} = \sqrt{\frac{\varepsilon''}{\varepsilon'}}$$

$$\frac{M_3}{M1} = \frac{\varepsilon''}{\sqrt{\varepsilon'}} \quad \text{...(18)}$$

2.5. Electric conductivity

$$\sigma = \omega \varepsilon_0 \varepsilon'' \quad \text{…(19)}$$

where, σ =electric conductivity

ω =phonon frequency.

2.6. Relaxation time (minimum)

Relaxation time (minimum) is,

$$\tau = \frac{\exp^{-(\frac{\pi}{2}\tan\delta)}}{\omega} \quad \text{…(20)}$$

2.7. Differentiability

$$SmoothFunction. = \frac{2\varepsilon''}{\pi\varepsilon} \quad \text{…(21)}$$

[III] RESULTS

We have calculated soft mode frequency, lattice frequency shift and width, dielectric constant, loss tangent, quality factor, acoustic attenuation, electric conductivity, relaxation time (min.), smooth function and ratio of figure of merits M_2/M_1, M_3/M_2, M_3/M_1 by using crystal constants given in table 1 and 2. Our all results (fig. 2-14) are in good agreement with experimental data.

Table: 1. Crystal constants of deuterated triglycine sulphate crystal.[30]

Physical constants	Numerical values for DTGS crystal
Ω (cm^{-1})	0.01
J (cm^{-1})	470
K (cm^{-1})	0
V_k ($cm^{-3/2}$)	15
T_c (K)	333.86
C (K)	4873.16
μ (10^{18}esu)	2.3
ħω (cm^{-1})	1.92

Table: 2. Calculated values of<S_1^x>, <S_2^x>, <S_1^z>, <S_2^z> for deuterated triglycine sulphate crystal.

T(K)	<S_1^x>	- <S_2^x>	<S_1^z>	- <S_2^z>
285	0.00021	0.0002	0.0025	0.00245
297	0.00043	0.000413	0.0022	0.00221
309	0.00045	0.000445	0.0018	0.00174
321	0.00046	0.00045	0.00125	0.00125
333	0.00047	0.00047	0	0
345	0.00044	0.000434	0	0
357	0.00042	0.000414	0	0
369	0.000425	0.000423	0	0
381	0.000423	0.00042	0	0
393	0.000421	0.000409	0	0

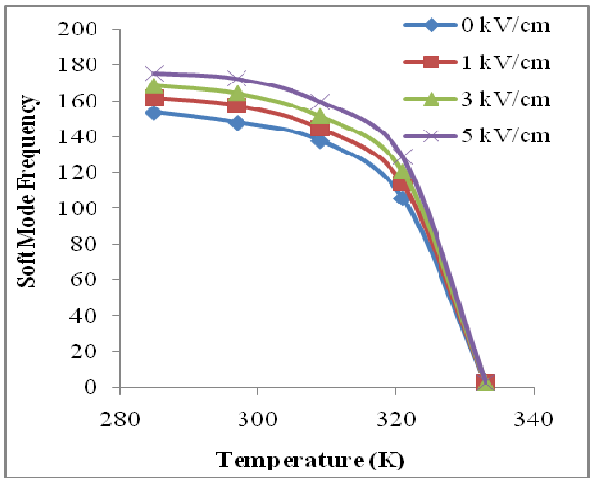

Fig: 2. Temperature and electric field dependent soft mode frequency of Fe-DTGS crystal.

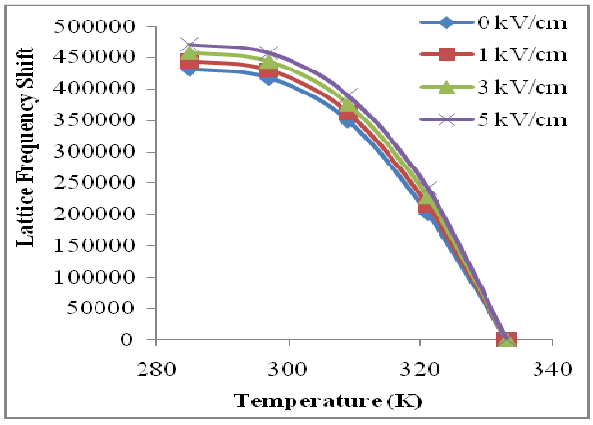

Fig: 3. Temperature and electric field dependent lattice frequency shift of Fe-DTGS crystal.

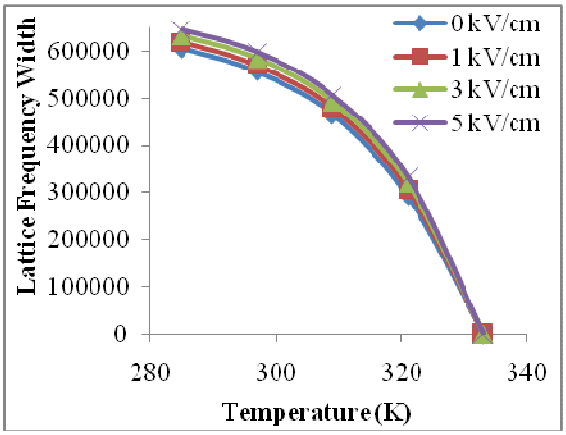

Fig: 4. Temperature and electric field dependent lattice frequency width of Fe-DTGS crystal.

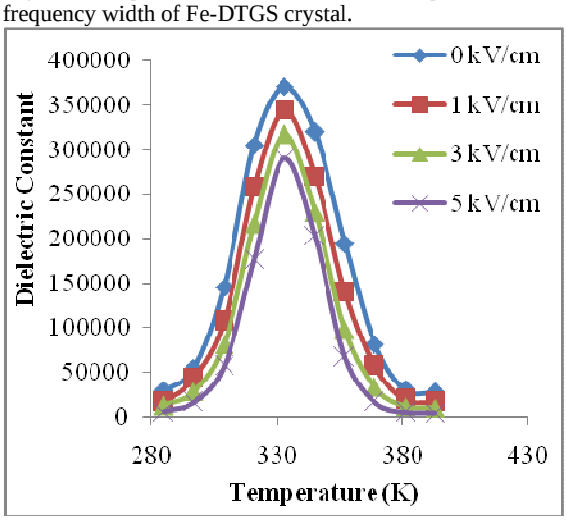

Fig: 5. Temperature and electric field dependent dielectric constant of Fe-DTGS crystal [33, 34].

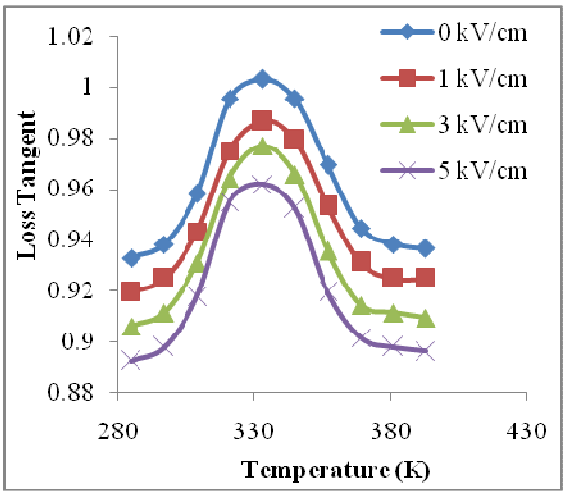

Fig: 6. Temperature and electric field dependent loss tangent of Fe-DTGS crystal [33, 34].

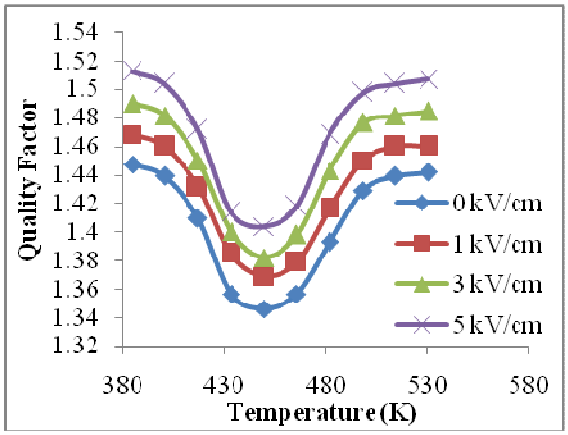

Fig: 7. Temperature and electric field dependent quality factor of Fe-DTGS crystal [33, 34].

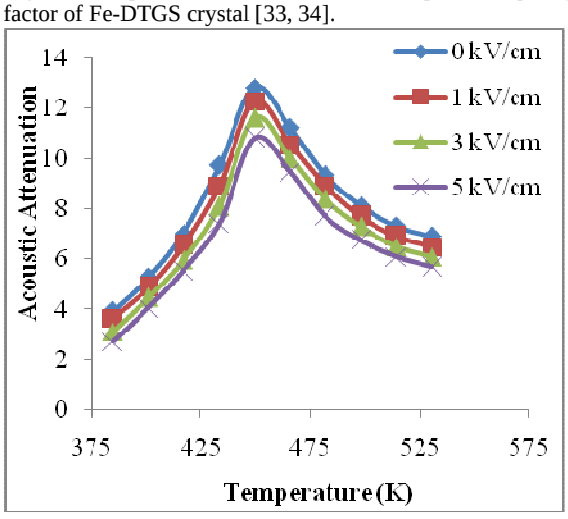

Fig: 8. Temperature and electric field dependent acoustic attenuation of Fe-DTGS crystal [35].

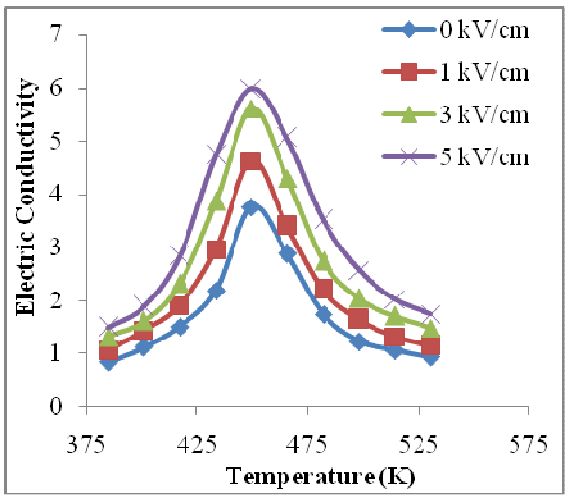

Fig: 9. Temperature and electric field dependent electric conductivity of Fe-DTGS crystal [4, 38].

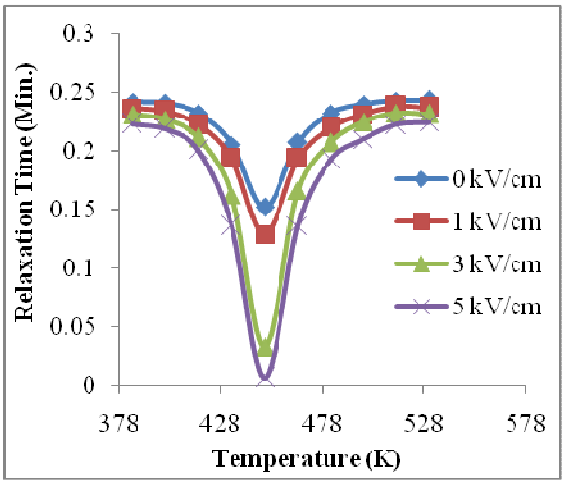

Fig: 10. Temperature and electric field dependent relaxation time of Fe-DTGS crystal [36].

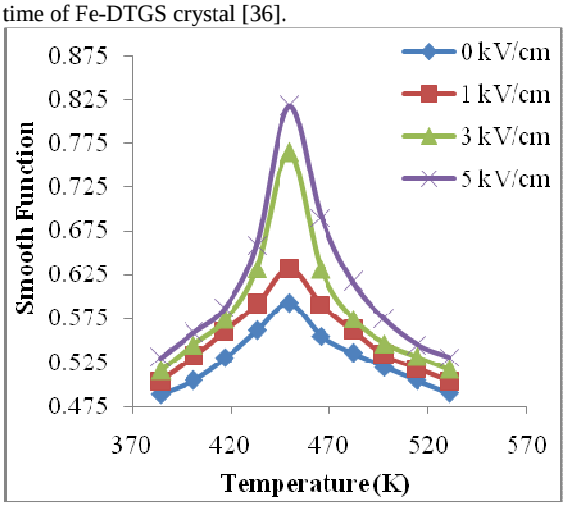

Fig: 11. Temperature and electric field dependent smooth function of Fe-DTGS crystal [37].

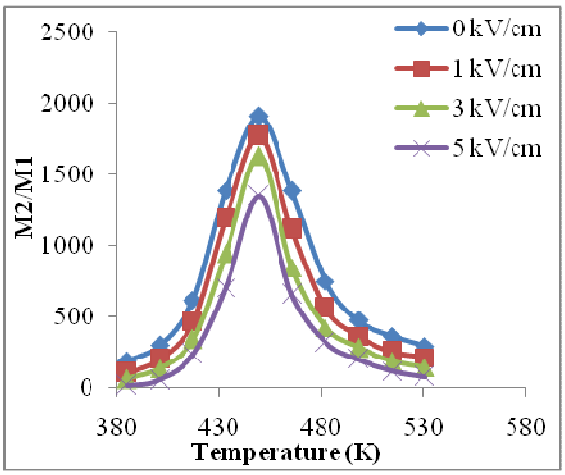

Fig: 12. Temperature and electric field dependent ratio of figure of merits (M_2/M_1) of Fe-DTGS crystal [28].

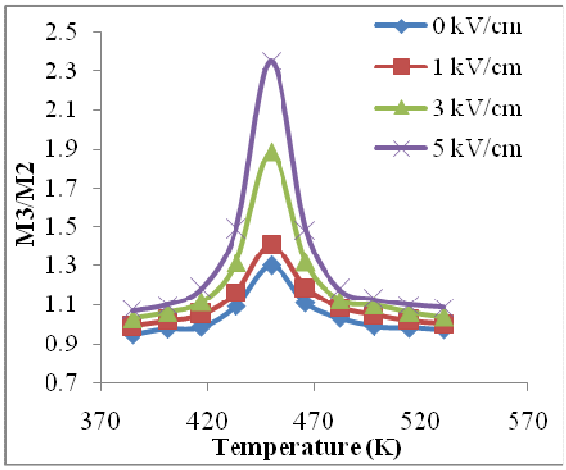

Fig: 13. Temperature and electric field dependent ratio of figure of merits (M_3/M_2) of Fe-DTGS crystal [28].

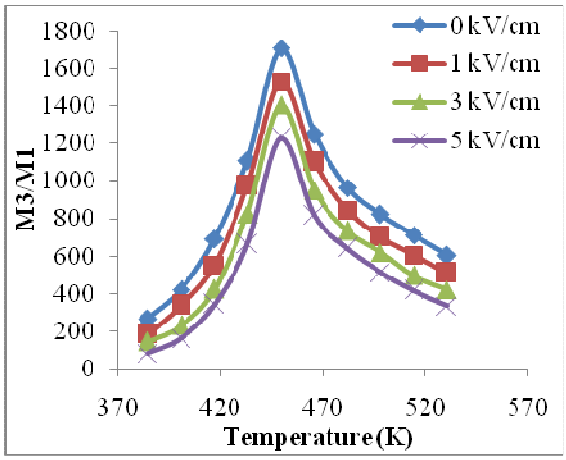

Fig: 14. Temperature and electric field dependent ratio of figure of merits (M_3/M_1) of Fe-DTGS crystal [28].

[IV] DISCUSSION

Our calculated results (fig. 2-14) are; soft model frequency of order 10^{-2}, lattice frequency shift and width of order 10^{-2}, dielectric constant of order 10^4 to 10^5, loss tangent of order 10^0, quality factor of order 10^0, acoustic attenuation of order 10^1, electric conductivity of order 10^0, relaxation time (min.) of order of 10^{-1} to 10^{-2}, smooth function of order 10^{-1}, and ratio of figure of merits M_2/M_1 of order 10^3, M_3/M_2 of order 10^0, $M_3/M_1$of order 10^3 at phase transition temperature (T_C). When we apply external electric field on the crystal then the corresponding characteristics changes as; soft mode frequency increases, lattice

frequency shift and width increases, dielectric constant decreases, tangent loss decreases, quality factor increases, acoustic attenuation decreases, electric conductivity increases, relaxation time decreases, smooth function increases, and ratio of figure of merits M_2/M_1decreases, M_3/M_2 increases, M_3/M_1 decreases with increasing order of electric fields. We have observed that increasing electric field slightly decrease the phase transition temperature (T_c). Our results show a high current response coefficient, vidicon sensitivity coefficient and infra-red detection coefficient which make this material very sensitive to infrared detection techniques. Fe-DTGS crystal is very useful material in construction of bi-stable ferroelectric memory and quantum state capacitors.

ACKNOWLEDGEMENT

Authors are grateful to Prof. R.P. Gairola (University Head of Physics Department, H.N.B.G.U., Srinagar Garhwal), Prof. P.K. Bajpai (Guru Ghasidas Univ., Bilaspur), Prof Shafikuddin Mollah (A.M.Univ., Aligarh), Prof. S.K. Srivastava (Bundel-khand Univ., Jhansi) and Prof. Ganga Saran (M.P.G. College, Mussoorie, India) for his kind suggestions and to Prof. U.C. Naithani (H.N.B.G.U., Pauri),Prof S.C Bhatt (H.N.B.G.U. Srinagar), Dr. Vinay Gupta (Delhi Univ.), Dr. K.S. Bartwal (R.R.C.A.T., Indore), Dr Shahid Hussain (A.M.U. Aligarh), Dr. K.K Verma (R.M.L. Avadh Univ. Faizabad), and Prof. K.N. Pathak FNA (P.U.,Chandigarh) for their encouragements.

REFERENCES

[1] Mathias B T, Miller C E, Remeika J P. [1956] Ferroelectricity of glycine sulphate, *Phys. Rev.*104(3):849-850.

[2] Pan-Lin Z, Qi-Wei Y, Zhi-Xu C and Yu-Fen C. [1986] Atomic postions of deuterium in DTGS crystal determined by neutron diffraction, *Acta Phys. Sin.* 35 (5):643-652.

[3] Strukov B A. [1966] Electrocaloric effect in monocrystalline triglycine sulphate. *Kristallografia* 11:892–95.

[4] Strukov BA, Taraskin SA, Varikash VM. [1968] Thermal and electrical properties of ferroelectric triglycine selenate near Curie point. *Fiz. Tverd. Tela* 10:1836–42.

[5] Strukov BA, Korzhuev MA, Baddur A, Koptsik VA. 1971. Spontaneous polarization of KH2PO4 single crystal near Curie point. *Fiz. Tverd. Tela* 13:1872–77.

[6] Strukov BA, Taraskin SA, Savilova ZV. 1986. Thermodynamical properties of diglycine nitrate (DGN) crystals. *Phys. Status Solid. A* 95:447–51.

[7] Strukov BA, Savilova ZV, Taraskin SA, Varikash VM. [1986]. Spontaneous polarization and electrocaloric effect in diglycine nitrate crystals in the phase transition region. *Fiz. Tverd. Tela* 28:733–38.

[8] Scott JF. [1989] On the theory of ferroelectric susceptibilities. *J. Phys. Soc. Jpn.* 58:4487–90.

[9] Scott JF. [1993] Dielectric properties of insulators. *In Encyclopedia of Applied Physics, ed. G Trigg* 5: 25–45. Berlin: VCH

[10] Flerov IN, Mikheleva EA. 2008. Electrocaloric effect and anomalous conductivity of the ferroelectric NH4HSO4. *Phys. Solid State* 50:478–84.

[11] Itoh K and Mitsui T. [1973] Studies of the crystal structure of triglycine sulphate in connection with its ferroelectric phase transition. *Ferroelectrics* 5(1):235-25.

[12] Kay MI and Klienberg R.[1973] The crystal structure of triglycine sulphate. *Ferroelectrics* 5(1):45-52.

[13] Lines ME and Glass AM.[1977] Principles of ferroelectrics and related materials. *Claren- don Press, Oxford* 321-327.

[14] Aravazhi S, Jeyavel R, Subramanian C. [1997] Growth and characterisation of benzophenone and urea doped triglycine sulphate crystals. *Ferroelectrics*, 200(1-4):279-286.

[15] Su G, Youping H, Hongshi Y, Zikong S, Qingin EJ.[2000] A new pyroelectric crystal L-lysine-doped TGS(LLTGS). *Cryst. Growth* 209(1):220-222.

[16] Gaffar MA, Abu El-Fadl A, Bin Anooz S.[2003] Influence of strontium doping on the indirect band gap and optical constants of ammonium zinc chloride crystals. *Physica B: Condensed Matter* 327(1):43-54.

[17] Sun D, Yu X, Gu Q. Growth kinetics and mechanism of TGS crystals.[1999] *Cryst. Res. Technol*.34(10):1255-1263.

[18] Brahadeeswaran S, Bhat HL, Kini NS, Umarji AM, Balaya P, Goyal PS.[2000] Dielectric, thermal and mechanical properties of the semiorganic nonlinear optical crystal sodium p-nitrophenolate dehydrate. *J. Appl. Phys.*88(10): 5935-5940.

[19] Erdei S, Jin BM, Bhalla AS, Ainger FW.[1995] Growth and characterisation of L-valine doped TGS single crystals. *Ferroelectrics* 174:289-301.

[20] Marcy HO, Rosker MJ, Warren LF, Cunningham PH, Thomas CA, DeLoach LA, Velsko SP, Ebbers CA, Liao JH, Kanatzidis MG.[1995] L-Histidine tetrafluoroborate: a solution-grown semiorganic crystal for nonlinear frequency conversion. *Opt. Lett.* 20(3):252-254.
[21] Abu El-Fadl A.[1999] Effect of divalent-ions-doping on the absorption spectra and optical parameters of triglycine sulphate crystals. *J. Phys. Chem. Solids* 60: 1881.
[22] Bhalla AS, Fang CS, Cross LE, Xi Y.[1984] Pyroelectric properties of the modified triglycine sulphate (TGS) single crystal. *Ferroelectrics* 54(1):151-154.
[23] Eisner J. [1978] The physical properties of TGS single crystals, grown from aqueous TGS solutions containing aniline. Ferroelectrics 17(1):575-578.
[24] Matthew FB, Jos O, Richard JS, Williams ER.[2008] Effects of alkaline earth metal ion complexation on amino acid zwitterions stability: Results from infrared action spectroscopy. *J. Am. Chem. Soc.*130(20):6463-6471.
[25] Cole M.[2003] Organic materials for second-harmonic generation: Advances in relating structure to function. *Phil. Trans. R. Soc. Lond. A* 361(1813):2751-2770.
[26] Theresita SN, Selvarajan P, Mahadevan CK.[2009] Growth, structural, mechanical, spectral and dielectric characterization of NaCl-added triglycine sulphate single crystals. *J. Curr. Appl. Phys*. 9(5):1155-1159.
[27] Batra AK, Aggarwal MD, and Lal RB.[2003] Growth and Characterization of Doped DTGS Crystals for Infrared Sensing Devices. *Mat. Lett*.57:3943–3948.
[28] Fang CS, Wang M and Zhuo HS.[1989] ADTGSP single crystal with high pyroelctric figure of merit. *Ferroelectrics* 91(1):373-377.
[29] Batra AK, Aggarwal MD, Lal RB.[2003] Growth and characterization of doped DTGS crystals for infrared sensing devices. *Materials Letters*:573943-3948.
[30] Chaudhuri BK, Chaudhari KR and Banerjee S.[1988] Green's-function theory of ferroelectric phase transitions in hydrogen-bonded triglycine sulphate with the pseudospin lattice coupled-mode model: A unified theory of structural phase transitions. II. Nonlinear properties, *Phys. Rev. B.*38(1):689.
[31] Gonzalo JA, Equation of state for the cooperative transition of triglycine sulphate near Tc, *Phys. Rev.* **B,**(1970), **1(7),**3125-3132.
[32] Zubarev DN, Double-time green functions in statistical physics, *Soviet Physics Uspekhi*,(1960)**3(3)**,320-345.
[33] Brezina B, Havrankova M, and Vasa M.[1992] Enhanced Growth of Non-Polar{001} Growth Sectors of Deuterated Triglycine Sulfate Doped With L-alanine (LADTGS). *Cryst. Res. Tech*. 27(1):13–20.
[34] Felix P, Gamot P, Lacheau P and Raverdy Y.[1978] Pyroelectric, dielectric & thermal properties of TGS, DTGS & TGFB. *Ferroelectrics* 17: 543-51.
[35] Shreekumar R and Philip J.[1994] Ultrasonic study of the para-ferroelectric phase transition in phosphate doped TGS crystals. *Ferroelectrics* 160(1):23-33.
[36] Ślósarek G, Idziak S, Piślewski N and Stankowski.[1982] nisotropy of the relaxation time T1 of NH_3 groups in triglycine sulphate crystals, J,*physic. Stat. solidi(b)*110(1):233-238.
[37] Dorogovtsev SN and Yushin NK.[2011] Acoustical properties of disordered Ferroelectrics. *Ferroelectrics* 112(1):27-44.
[38] Gaffar M A, Al-Houty L I and Al-Muraikhi M.[1987] The dffect of doping crystals of TGS with some di- and trivalent ions on its: (I) dielectric constant and A.C. conductivity. *Qatar Univ.Sci.Bull.***7:**39-53.