Electric Conductivity, Permittivity (Capacitance), Acoustic Loss and Quality Factors of Triglycine Sulphate Crystal (Isomorphs) with External Biasing†

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In external biasing, electric capacitance (permittivity), quality factor, acoustic attenuation and electric conductivity of pyroelectric, triglycine sulphate crystal (TGS) whose chemical structure is $(NH_2CH_2COOH)_3H_2SO_4$. This centrio-symmetric crystal and its isomorphs have been studied by two sub-lattice pseudospin lattice coupled mode (PLCM) model or vibration model which is extended with third and fourth order phonon an-harmonic interaction and electric field terms. In-homogeneity of this pseudospin lattice coupled mode model has been solved by the use of double time, temperature dependent Green's function with renormalized boundary conditions. For better results in dielectric permittivity (capacitance), quality factor, electric conductivity and acoustic attenuation of triglycine sulphate crystal we combine pseudospin lattice coupled mode model with a different theoretical model that is Ising spin model of ferroelectrics. By the collaboration of these two theoretical models, we can predict about, physical and physio-chemical properties of triglycine sulphate crystal with best experimental supports.

Key Words: Pseudo spin-phonon, An-harmonic interaction, Green's function, Monoclinic.

INTRODUCTION

Triglycine sulphate crystal (TGS)[1] is a hydrogen bonded, pyroelectric, order-disorder type ferroelectric crystal[2-6] which exhibit a spontaneous polarization at room temperature. Chemically it is made by, three molecules of glycine and one molecule of sulphuric acid with uniaxial phases $[3HN_2CH_2COOH + H_2SO_4 \longrightarrow (NH_2CH_2COOH)_3H_2SO_4]$. Triglycine sulphate exhibits a phase transformation at 49 ºC (322.6 K) from polar phase to non-polar phase. Triglycine sulphate crystal is a monoclinic 2m, m/2 type centrio-symmetric crystal which consist of glycine ions. Glycine ion has three possible configurations in the crystal (glycine I, II and III). Among these three glycine ions, glycine I is a coplanar type ion, while glycine II and glycine III are quasi planar ions with some displaced nitrogen atom from carbon and oxygen atom plane, although they have a mirror symmetry. Thus these two mirror symmetric ions (glycine II and glycine III) form a double potential well system. This double potential well system of triglycine sulphate crystal trap an asymmetric type hydrogen bond in itself which caused, a phenomenon of pseudo-spin or order-disorder type behaviour of the proton (hydrogen bond) in the crystal[7]. This is why triglycine sulphate crystal has got

a very special and miracle features in condensed matter physics. During our study, we deal with all these special features of triglycine sulphate crystal. For this purpose of study we deal with PLCM model (pseudospin lattice coupled mode model)[8-10] extended with two sub-lattice mode as well as third and fourth order phonon an-harmonic interaction terms and electric field terms[11-15] in company with double time, temperature dependent Green's function[16] under renormalized boundary conditions of polarization. With PLCM model we take a help from a different theoretical model that is Ising spin model[17] of ferro-electrics for better explanation about triglycine sulphate crystal even in external electric field biasing (DC). Thus in this way we study about the dielectric permittivity, quality factor, electric conductivity and acoustic attenuation of triglycine sulphate crystal[18-20] even in external electric biasing (DC). We also deal with the study of doped type triglycine sulphate crystal which is known as, an isomorphs of the crystal. Our study about these isomorphs of triglycine sulphate crystal says that "these isomorphs of triglycine sulphate crystal show same type of behaviour as pure triglycine sulphate crystal but respective data for isomorphs is slightly different than pure type". This difference of data depends on the nature of doped impurity in the crystal. In both cases our results have best

experimental support[18-20]. At conclusion, we can predict that triglycine sulphate crystal is very useful in sensor/detector technology, nano-technology, computing technology and also in renewable energy techniques which predict about the role of triglycine sulphate crystal in agriculture, space, geo and medical science, *etc*.

THEORETICAL STUDIES

Theoretical methods: We use a theoretical model which consider anharmonic interactions of lattice vibration accompany with Ising spin model of ferroelectrics, never done before for hydrogen bonded triglycine sulphate crystal in ferroelectric class with external DC (direct current) biasing by any other authors. These all theoretical model's calculation predicts the best mechanism of crystal behaviour.

Model Hamiltonian: For triglycine sulphate crystal we have, extended two-sublattice pseudospin-lattice coupled mode model[4] with third and fourth order phonon anharmonic interaction terms as well as external electric field term which is expressed as:

$$H = -2\Omega \sum_i \left(S_{1i}^x + S_{2i}^x\right) - \sum_{ij} J_{ij}\left[\left(S_{1i}^z S_{2i}^z\right) + \left(S_{2i}^z S_{2i}^z\right)\right]$$
$$- \sum_{ij} K_{ij}\left(S_{1i}^z S_{2i}^z\right) - 2\mu E \sum_i \left(S_{1i}^z + S_{2i}^z\right)$$
$$+ \frac{1}{4}\sum_k \omega_k \left(A_k A_k^+ + B_k B_k^+\right) - \sum_{ik} V_{ik} S_{1i}^z A_k - \sum_{ik} V_{ik} S_{2i}^z A_k^+$$
$$+ \sum_{k_1 k_2 k_3} V^{(3)}\left(k_1, k_2, k_3\right) A_{k_1} A_{k_2} A_{k_3}$$
$$+ \sum_{k_1 k_2 k_3 k_4} V^{(4)}\left(k_1, k_2, k_3, k_4\right) A_{k_1} A_{k_2} A_{k_3} A_{k_4} \quad (1)$$

where in eqn. 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[15] and Green's function, width, shift and soft mode frequency of the crystal is, we consider the Green's function

$$G_{ij}(t-t') = \left\langle\left\langle S_{1i}^Z(t); S_{1j}^Z(t')\right\rangle\right\rangle$$
$$= -i\theta(t-t')\left\langle\left[S_{1i}^Z(t); S_{1j}^Z(t')\right]\right\rangle \quad (2)$$

in which $\theta(t-t')$ step function is zero for $t < t'$ and unity for $t > t'$. The angular bracket <.....> denotes ensemble average over a grand canonical ensemble. Differentiated twice GF(2) first with respect to time(t) and then with respect to time (t') using model Hamiltonian (eqn. 1) taking fourier transformation and setting it into Dyson's equation from

$$G_{ij}(\omega) = G_{ij}^0(\omega) + G_{ij}^0(\omega) P(\omega) G_{ij}^0(\omega) \quad (3)$$

where,
$$G_{ij}^0(\omega) = \frac{\Omega\langle S_{1i}^x\rangle \delta_{ij}}{\pi(\omega^2 - 4\Omega^2)} \quad (4)$$

where,
$$G_{ij}(\omega) = \frac{\Omega\langle S_{1i}^x\rangle}{\pi(\omega^2 - 4\Omega^2 - P(\omega))} \quad (5)$$

where,
$$P(\omega) = \tilde{P}(\omega) + \tilde{\tilde{P}}(\omega), \quad (6)$$

$$\tilde{P}(\omega) = \frac{\pi i}{\Omega\langle S_{1i}^x\rangle^2}\left\langle F_i^{(t)}; S_{ij}^y\right\rangle \quad (7)$$

and,
$$\tilde{\tilde{P}}(\omega) = \frac{\pi^2}{\Omega^2\langle S_{1i}^x\rangle^2}\left\langle\left\langle F_i, F_j\right\rangle\right\rangle \quad (8)$$

The second term of eqn. 6 contains higher order Green's functions which are decoupled by using scheme <abcd> = <ab> <cd> + <ac> <bd> + <ad> <bc>. Then simpler Green's functions are solved in the zeroth order approximation *i.e.* higher order terms are neglected from $P(\omega)$ type terms. In eqn. 8 $\tilde{\tilde{P}}(\omega)$ is resolved into its real and imaginary parts using formula . The real part is known as shift and the imaginary part is called width $\Gamma(\omega)$. These are obtained as following: Spin shift is,

$$\Delta_s(\omega) = \frac{a^4}{2\Omega(\omega^2 - \tilde{\Omega}^2)} + \frac{b^2 c^2}{4\Omega\tilde{\Omega}} + \frac{V_{jk}^2 N_k a^2}{2\Omega(\omega^2 - \tilde{\Omega}^2)} + \frac{4\mu^2 E^2 a^2}{2\Omega(\omega^2 - \tilde{\Omega}^2)} \quad (9)$$

$$\Delta_{s-p}(\omega) = \frac{2V_{ik}^2\langle S_{1i}^x\rangle \omega_k \delta_{kk^i} \left(\omega^2 - \tilde{\tilde{\omega}}_k^2\right)}{\left[\left(\omega^2 - \tilde{\Omega}_k^2\right)^2 + 4\omega_k^2\Gamma_k^2(\omega)\right]} \quad (10)$$

Spin width is

$$\Gamma(\omega) = \frac{\pi a^4}{4\Omega\tilde{\Omega}}\left[\delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega})\right]$$
$$+ \frac{b^2 c^2}{4\Omega\tilde{\Omega}}\left[\delta(\omega - \tilde{\Omega}) - (\omega + \tilde{\Omega})\right]$$
$$\frac{V_{ik}^2 N_k a^2}{4\Omega\tilde{\Omega}}\left[\delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega})\right] +$$
$$\frac{2\pi\mu^2 E^2 a^2}{4\Omega\tilde{\Omega}}\left[\delta(\omega - \tilde{\Omega}) - \delta(\omega + \tilde{\Omega})\right] \quad (11)$$

Spin phonon width is

$$\Gamma_{s-p}(\omega) = \frac{4V_{ik}^2\langle S_{1i}^x\rangle \omega_k\left(\omega^2 - \tilde{\tilde{\omega}}_k^2\right)}{\left[\left(\omega^2 - \tilde{\tilde{\omega}}_k^2\right)^2 + 4\omega_k^2\Gamma_k^2(\omega)\right]} \quad (12)$$

In enqs. 10 and 12 $\tilde{\omega}_k$ is renormalized phonon frequency and $\Gamma_k(\omega)$ is phonon width in the Green's function $G_{kk'}(t-t') = <<A_k(t); A_{k^1}(t')>>$ which are obtained as:2

$$G_{ij'}(\omega) = \frac{\omega_k \delta_{kk'}}{\pi\left[\omega^2 - \tilde{\tilde{\omega}}_k^2 - 2\omega_k\{\Delta_k(\omega) + i\Gamma(\omega)\}\right]} \quad (13)$$

$$\widetilde{\widetilde{\omega}}_k^2 = \widetilde{\omega}_k^2 + 2\omega_k\Delta_k(\omega) \quad (14a)$$

Phonon shift is given as:

$$\Delta_k(\omega) = \operatorname{Re} P_k(\omega)$$
$$= 18P\sum_{k_1k_2}\left|V^{(3)}(k_1, k_2, -k)\right|^2$$

$$\frac{\omega_{k1}\omega_{k2}}{\widetilde{\omega}_{k1}\widetilde{\omega}_{k2}}\left\{(n_{k1}+n_{k2})\frac{\widetilde{\omega}_{k1}+\widetilde{\omega}_{k2}}{\omega^2-(\widetilde{\omega}_{k1}+\widetilde{\omega}_{k2})^2}\right.$$

$$\left.+(n_{k_2}-n_{k_1})\frac{\widetilde{\omega}_{k1}+\widetilde{\omega}_{k2}}{\omega^2-(\widetilde{\omega}_{k1}+\widetilde{\omega}_{k2})^2}\right\}$$

$$+48P\sum_{k_1k_2k_3}\left|V^{(4)}(k_1k_2, k_3, -k)\right|^2\frac{\omega_{k_1}\omega_{k_2}\omega_{k3}}{\widetilde{\omega}_{k_1}\widetilde{\omega}_{k_2}\widetilde{\omega}_{k3}}$$

$$\left\{(1+n_{k_1}n_{k_2}+n_{k_2}n_{k_3}+n_{k_3}n_{k_1})\frac{\widetilde{\omega}_{k_1}+\widetilde{\omega}_{k_2}+\widetilde{\omega}_{k_3}}{\omega^2-(\widetilde{\omega}_{k_1}+\widetilde{\omega}_{k_2}+\widetilde{\omega}_{k_3})^2}\right.$$
$$+3(1-n_{k_2}n_{k_1}+n_{k_2}n_{k_3}-n_{k_3}n_{k_1})$$

$$\left.\frac{\widetilde{\omega}_{k_1}+\widetilde{\omega}_{k_2}+\widetilde{\omega}_{k_3}}{\omega^2-(\widetilde{\omega}_{k_1}+\widetilde{\omega}_{k_2}+\widetilde{\omega}_{k_3})^2}\right\} \quad (14b)$$

and phonon width is given as:

$$\Gamma_k(\omega) = \operatorname{Im} P_k(\omega)$$
$$= 9\pi\sum_{k_1k_2}\left|V^{(3)}(k_1, k_2, -k)\right|^2\frac{\omega_{k_1}\omega_{k_2}}{\widetilde{\omega}_{k_1}\widetilde{\omega}_{k_2}}$$
$$\left\{(n_{k_1}+n_{k_2})\left[\delta(\omega+\widetilde{\omega}_{k_1}+\widetilde{\omega}_{k_1})\right]\right.$$

$$-\delta(\omega-\widetilde{\omega}_{k_1}-\widetilde{\omega}_{k_1}) + (\text{higher terms})$$

$$\left.+(n_{k_2}-n_{k_1})[\delta(\omega+\widetilde{\omega}_{k_1}+\widetilde{\omega}_{k_2})-\delta(\omega+\widetilde{\omega}_{k_1}+\widetilde{\omega}_{k_2})]\right\}$$

$$+48\pi\sum_{k_1k_2k_3}\left|V^{(4)}(k_1, k_2, k_3, -k_4)\right|^2\frac{\omega_{k_1}\omega_{k_2}\omega_{k_3}}{\widetilde{\omega}_{k_1}\widetilde{\omega}_{k_2}\widetilde{\omega}_{k_3}}$$

$$X\left\{(1+n_{k_1}n_{k_2}+n_{k_2}n_{k_3}+n_{k_3}n_{k_4})\right.$$

$$X[\delta(\omega+\widetilde{\omega}_{k_1}+\widetilde{\omega}_{k_2}+\widetilde{\omega}_{k_3})-\delta(\omega-\widetilde{\omega}_{k_1}-\widetilde{\omega}_{k_2}-\widetilde{\omega}_{k_3})]$$

$$+3(n_{k_1}n_{k_2}+n_{k_2}n_{k_3}-n_{k_3}n_{k_4})+3(n_{k_1}n_{k_2}+n_{k_2}n_{k_3}-n_{k_3}n_{k_4})$$

$$\left.X[\delta(\omega+\widetilde{\omega}_{k_1}-\widetilde{\omega}_{k_2}-\widetilde{\omega}_{k_3})-\delta(\omega-\widetilde{\omega}_{k_1}+\widetilde{\omega}_{k_2}+\widetilde{\omega}_{k_3})]\right\} \quad (14c)$$

$$\widetilde{\widetilde{\omega}}_k^2 = \widetilde{\omega}_k^2 + A_k(T) \quad (14d)$$

The Green's function (2) finally becomes,

$$G_{ij}(\omega) = \frac{\Omega\langle S_{1i}^x\rangle\delta_{ij}}{\pi(\omega^2-\hat{\Omega}^2-P(\omega))}, \text{ and, } \hat{\Omega}^2 = \widetilde{\widetilde{\Omega}}^2 + 2\Omega\Delta_{s-p}(\omega) \quad (15)$$

$$\widetilde{\widetilde{\Omega}}^2 = \widetilde{\Omega}^2 + 2\Omega\Delta_s(\omega) \text{ and } \widetilde{\Omega}^2 = 4\Omega^2 + \frac{1}{\Omega\langle S^{x}{}_{1i}\rangle}\langle[F, S_{1j}{}^y]\rangle \quad (16)$$

In eqn. 18 second term is evaluated using mean field approximation *i.e.*

$$\frac{\langle S_{1i}^z\rangle}{a} = \frac{\langle S_{1i}^x\rangle}{b} = \frac{1}{2\widetilde{\Omega}}\tanh\beta\frac{\widetilde{\Omega}}{2} \quad (17)$$

which gives, $\widetilde{\Omega}^2 = a^2 + b^2 + bc$ and

$$a = 2J\langle S_1^z\rangle + K\langle S_2^z\rangle + 2\mu E \text{ and } b = 2\Omega \quad (18)$$

and $c = 2J\langle S_1^x\rangle + K\langle S_2^x\rangle$ Solving, eqn. 16

$$\hat{\Omega}_\pm^2 = \frac{1}{2}\left(\widetilde{\widetilde{\omega}}_k^2 + \widetilde{\widetilde{\Omega}}^2\right) \pm \frac{1}{2}\left[\left(\widetilde{\widetilde{\omega}}_k^2 - \widetilde{\widetilde{\Omega}}^2\right)^2 + 8V_{ik}^2\langle S_{1i}^x\rangle\Omega\right]^{1/2} \quad (19)$$

$$T_c = \frac{\eta}{2k_B\tanh^{-1}\left(\dfrac{\eta^3}{4\Omega^2J^*}\right)},$$

where, $\eta^2 = (2J-K)^2\sigma^2 + 4\Omega^2 + (2\mu E)^2 \quad (20)$

and $\quad (J+K)* = (2J+K) + \dfrac{2V_{ik}^2\widetilde{\omega}_k^2}{\left[\widetilde{\omega}_k^4 + 4\omega_k\Gamma_k^2\right]}$

J* is renormalized exchange interaction constant.

Dielectric constant and Loss tangent

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

$$\chi(\omega) = -\lim_{X\to0}2\pi N\mu^2 G_{ij}(\omega+iX) \quad (21)$$

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

$$\in = 1 + 4\pi\chi \quad (22)$$

With the help of eqn. 25 and 26 one obtain expression for dielectric constant as:

$$\in(\omega) = (-8\pi N\mu^2)\frac{\langle S_1^x\rangle\Omega}{\left[(\omega^2-\hat{\Omega}^2)^2 + 4\Omega^2\Gamma^2\right]} \quad (23)$$

$\in(\omega) \gg 1$ 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

$\tan\delta = \dfrac{\in''}{\in'}$, by using eqn. 30 and 31 we obtains expression for

loss tangent as $\tan\delta = -\dfrac{2\Omega\Gamma(\omega)}{(\omega^2-\hat{\Omega}^2)}$, Acoustic attenuation:

$\alpha = \dfrac{\Gamma(\omega)}{\nu}$, where $\Gamma(\omega)$ = width, ν = sound velocity and Q-

Factor = 1/tan δ, while electric conductivity: $\sigma = \omega$?" (24)

General procedure: We have a theoretical calculation method in which we substitute literatures values from an Ising spin model to PLCM model of ferroelectrics.

Detection method: Match with ours theoretical data perfectly with experimental results performed by some other authors.

RESULTS AND DISCUSSION

Graphs: By using model values from literatures (Table-1), we calculate theoretical results for temperature and electric

TABLE-1 MODEL VALUES OF PHYSICAL PARAMETERS FOR TRIGLYCINE SULPHATE CRYSTAL									
ω_0^2 (cm^2)	Ω (cm^{-1})	J (cm^{-1})	K (cm^{-1})	V_{ik} (cm$^{-3/2}$)	T_C (K)	C (K) (cm^{-1})	N_μ (10^{18} esu)	A_k	B_0
0.59	0.1	340	0	10	49.1	3007	2.22	10.2	0

field (DC) dependent dielectric permittivity (capacitance), quality factor, electric conductivity and acoustic attenuation of triglycine sulphate crystal are shown in Figs. 1-4.
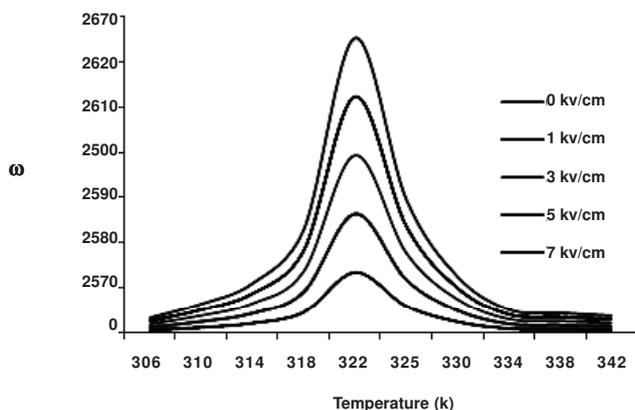
Fig. 1. Temperature dependent dielectric permittivity (capacitance) of triglycine sulphate crystal in presence of electric field
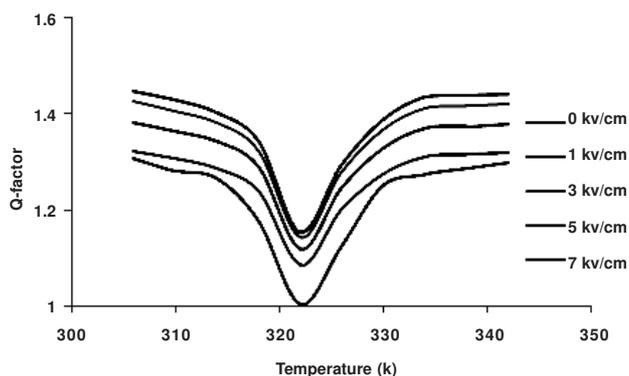

Fig. 2. Temperature dependent quality factor of triglycine sulphate crystal in presence of electric field
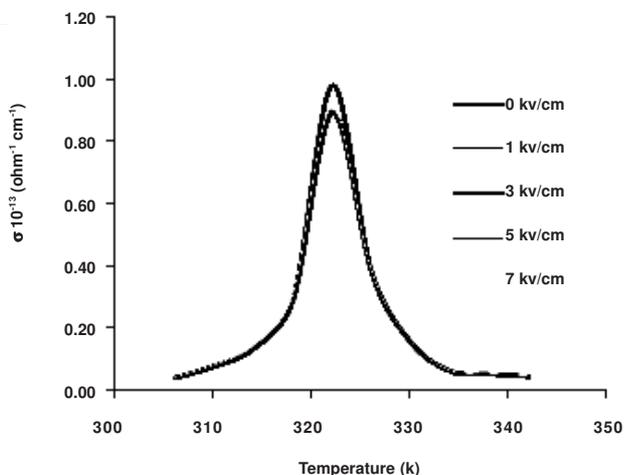

Fig. 3. Temperature dependent electric conductivity of triglycine sulphate crystal in presence of electric field
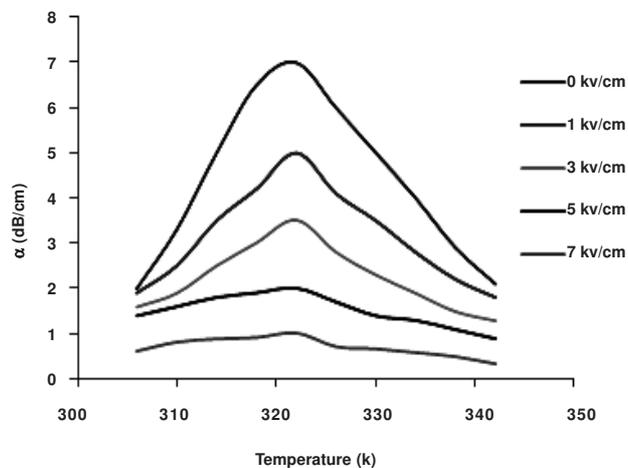

Fig. 4. Temperature dependent acoustic attenuation of triglycine sulphate crystal in presence of electric field

This study reveals the real and imaginary parts (ε' and ε'') of dielectric permittivity and dielectric loss ($\varepsilon''/\varepsilon'$) of triglycine sulphate crystal. At the same time quality factor, electric conductivity and acoustic attenuation of crystal is also evaluated, although it is exposed in the external electric field (DC). For this purpose of study, we use a theoretical model which is known as PLCM model extended with two sub-lattice mode as well as third and fourth order phonon anharmonic interaction terms which is never considered before by any other author, provide a much-more exact explanation about crystal behaviour. This model works with double time temperature dependent Green's function for second order phase transition in renormalized boundary conditions of polarization. Ising spin model gives a much more liability to this PLCM model. All these features of PLCM model suits with triglycine sulphate crystal conditions and works perfectly in a better way than any other model. This is the reason that our results have greater accuracy and best agreement with actual conditions. Permittivity at transition temperature is greatest and it decreases with ascending order of external electric field (DC) while quality factor of triglycine sulphate crystal has minimum value at transition temperature but it increases with ascending order of external electric field (DC). Electric conductivity of triglycine sulphate crystal is directly proportion to imaginary part of permittivity which tends to a highest value at transition temperature which decreases with ascending order of electric field and acoustic attenuation decreases with ascending order of electric field at transition temperature. We have also observed that transition temperature is slightly decreases with external electric field (DC) in ascending order of values. Same result comes for lightly doped triglycine sulphate crystal which is known as isomorphs of triglycine sulphate crystal but theoretical results for isomorphs is a little bit different than pure type. In both cases our results have best agreement with experimental data.

Conclusion

Pseudospin lattice coupled mode (PLCM) for triglycine sulphate crystal explains more reliable results compare to any other model. Ising model provide to this model more stability and accuracy. That's why we have best experimental support. Not only for this crystal but also for the isomorphs of this crystal and many other crystals, this model may have a best application in hydrogen bonded pseudo type materials.

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