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Study of Ferroelectric Phase Transition in Triglycine Selenate Crystal

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Abstract: Triglycine selenate (TGSe) is a Hydrogen bondend order disorder type ferroelectric, which go through a structural phase transition at T_c=295K. TGSe is very similar to the Triglycine Sulphate crystal, which is extensively used in infrared detection. In the present paper we are using double time thermal Green's function method and modified pseudospin model to discuss ferroelectric behavior of TGSe crystal. Expressions for shift, width, soft mode frequency, dielectric constant, loss and transition temperature have been evaluated. By fitting model values of physical quantities in the theoretical expressions thermal dependence of soft mode frequency, dielectric constant and loss have been calculated in the vicinity of transition temperature. Theoretical results are in well agreement with experimental results of other researchers.

Keywords: TGSe, Ferroelectric, Dielectric Constant, Soft mode frequency, Tangent loss

Introduction

The Triglycine selenate [$(NH_2CH_2COOH)_3H_2SeO_4$, abridged as TGSe] belongs to a very interesting set of hydrogen bonded ferroelectrics and bears a close resemblance to vastly studied TGS family. TGSe crystals go through a archetypical order-disorder phase transition at about T_c~295K. This transition from paraelectric phase to ferroelectric phase is associated with transformation in space group symmetry from $P2_1/m$ to $P2_1$. Lattice parameters for TGSe are a=9.54Å, b=12.92Å, c=5.86Å and β =110°.

TGSe crystals have similar space group symmetries as of TGS crystal [Kay and Kleinberg 1973]. There are various other similarities found by various researchers [Itoh and Mitsui 1973,Choudhury and Chitra et. al. 2004, Balasubramanian and Krishnan 1963] between these two crystals. In both crystals, molecular units from the viewpoint of the structural ferroelectric phase transition are $-NH_3^+$ group connected with one of the three glycine ions and the hydrogen bond between the residual glycine ions [Balasubramanian and Krishnan 1963]. The most important discrepancy between the structure of TGSe and TGS is bearing of SeO_4^+ group instead of SO_4^+ group. As a result of this its specific heat peak is six times larger in comparison with TGS [Ema 1983,Noheda and Lifante et. al. 1993]. Some properties of these crystals depend on the specifications of their growing techniques [Sirota and Tsedrik 1971] but the crystal does not show enormous change due to this. The Phase transition in TGSe crystals are analyzed by various researchers using different methods such as high sensitivity calorimetric

technique [Romero and Gallardo et. al. 2004, Romero and Gallardo et. al. 2006], linear birefringence method [Iglesias and Castillo 1998, Przeslawski 2000].

Theoretical studies regarding TGSe type ferroelectric have been carried out by Chaudhuri and Choudhury et. al (1988) by taking psuedospin lattice coupled mode model as a tool. In present paper we are modifying this model to produce better and convincing results. This paper include loss tangent graph and some new formulas which were not present in our earlier paper [Khanduri and Upadhyay 2017] .

Outline of our paper is as follows. First with the help of Green's function approach we obtain the expressions for shift, width, soft mode frequency, dielectric constant, tangent loss and transition temperature in section 2. In the succeeding section we explain and discuss about results and obtained formulas in section 2. Our paper is accomplished with a conclusion in section 4.

Calculation

In present study to explain phase transition of TGSe crystal, the Hamiltonian used is

$$H = -2\Omega\sum_i (S_{1i}^x + S_{2i}^x) - \sum_{ij}[J_{ij}(S_{1i}^z S_{1j}^z + S_{2i}^z S_{2j}^z) + K_{ij}S_{1i}^z S_{2j}^z] - \sum_k V_{ik}(S_{1i}^z A_k + S_{2j}^z A_k^\dagger) + \frac{1}{4}\sum_k \omega_k (A_k^\dagger A_k + B_k^\dagger B_k)$$
$$+ \sum_{k_1k_2k_3} V^{(3)}(k_1,k_2,k_3) A_{k_1} A_{k_2} A_{k_3} + \sum_{k_1k_2k_3k_4} V^{(4)}(k_1,k_2,k_3,k_4) A_{k_1} A_{k_2} A_{k_3} A_{k_4} - \sum_{ik} V_{ik} S_{1i}^x A_k - \sum_{ik} V_{ik} S_{2i}^x A_k^\dagger$$

where Ω is proton tunneling frequency, J and K are coupling constants corresponding to coupling in same lattice and different lattices respectively, V_{ik} is spin-lattice interaction constant, ω_k is phonon frequency, S^z and S^x are components of pseudospin variable S, A_k and B_k are operators corresponding to position and momenta, $V^{(3)}(k_1,k_2,k_3)$ are $V^{(4)}(k_1,k_2,k_3,k_4)$ third and fourth order atomic force constants.

This Hamiltonian is modified pseudospin lattice coupled mode model. For modifying model we are introducing here third and fourth order phonon anharmonic interaction and extra spin-lattice coupling terms. Introduction of anharmonic terms leads to explanation of dynamic characteristics of TGSe and extra spin-lattice coupling is an indirect coupling between tunneling motion of one proton and other proton, which modulates distance between two equilibrium sites in O–H··O bonds.

We shall evaluate double time thermal Green's function given below

$$G_{ij}(t-t') = \left\langle\left\langle S_i^z(t); S_j^z(t')\right\rangle\right\rangle = -i\theta(t-t')\left\langle\left[S_i^z(t), S_j^z(t')\right]\right\rangle \quad (1)$$

where angular brackets denote the average over the grand canonical ensemble and $\theta(t-t')$ is the Heaviside's step function which is 1 for $(t-t')$ greater than 0 or 0 otherwise. We differentiate Green's function mentioned above twice with respect to times t and t', then Fourier transforming and putting into Dyson's equation form

$$G_{ij}(\omega) = G_{ij}^{0}(\omega) + G_{ij}^{0}(\omega)\tilde{P}(\omega)G_{ij}^{0}(\omega) = G_0(\omega) + G_0(\omega)\tilde{\pi}(\omega)G_0(\omega)$$

we get a Green function which contains higher order Green's function and simpler Green's function. Higher order Green's functions are evaluated by decoupling schemes while simple Green's functions by Zeroth order approximation. The Green's function which we at last obtain by this procedure is

$$G_{ij}(\omega) = \frac{\Omega\langle S_{1i}^{x}\rangle}{\pi\left[\omega^2 - \hat{\Omega}^2 - 2i\Omega\Gamma(\omega)\right]} \tag{2}$$

where $\hat{\Omega}^2 = \left(2J\langle S_1^z\rangle + K\langle S_2^Z\rangle\right)^2 + 4\Omega^2 - 4J\Omega\langle S_1^X\rangle - 2\Omega K\langle S_2^X\rangle + \Delta(\omega)$

From Eq (2) it is clear that final Green's function contain Shift $\Delta(\omega)$ and width $\Gamma(\omega)$. Formula for these two is given in our previous paper [Khanduri P C and Upadhyay T C 2017].

Solving Eq (2) self consistently we obtain

$$\hat{\Omega}^2 = \frac{1}{2}(\tilde{\tilde{\omega}}_k^2 + \tilde{\tilde{\Omega}}^2) \pm \frac{1}{2}\left[(\tilde{\tilde{\omega}}_k^2 - \tilde{\tilde{\Omega}}^2)^2 + 4\left\{\begin{array}{l} 4\Omega^2 V_{ik}^2\langle S_1^x\rangle\omega_k + \dfrac{8\Omega a V_{ik}^2\langle S_1^z\rangle\omega_k}{b} + \\ \dfrac{2V_{ik}^2 J_{ij}^2\langle S_1^x\rangle\langle S_1^z\rangle^2\omega_k + V_{ik}^2 J_{ij}^2\langle S_1^x\rangle\langle S_1^z\rangle^2\omega_k}{\Omega} \\ + \dfrac{2V_{ik}^4\langle S_1^x\rangle N_k\omega_k}{\Omega} + \dfrac{2aV_{ik}^4\langle S_1^z\rangle N_k\omega_k}{b\Omega} \end{array}\right\}\right]^{1/2} \tag{3}$$

In above equation the frequency corresponding to negative sign is soft mode frequency. From above equation it is clear that soft mode frequency depends explicitly on phonon frequency as well as spin lattice interaction terms.

The soft mode frequency approaches to zero, when the phase transition temperature is approached, which ultimately determine the limit of the paraelectric phase. The soft mode frequency can be expand in the power of $(T-T_C)$ around its value at T_C, when temperature reaches near transition temperature, which yields

$$\hat{\Omega}_{-}^2 = \frac{\Omega^2\tilde{J}(0)}{2k_B T_C^2}\sec h^2\left(\frac{\Omega}{2k_B T_C}\right)(T-T_c) = K(T-T_C) \tag{4}$$

Where k_B is the Boltzmann's constant T_C is evaluated from Eq. (4) by using the lattice instability condition i.e. soft mode frequency approaches zero at the transition temperature, T_C. This condition gives

$$T_c = \frac{\eta}{2k_B \tanh^{-1}\left(\frac{\eta^3}{4\Omega^2 \tilde{J}_{ij}}\right)}, \quad (5)$$

Where $\eta^2 = (2J_0 - K_0)^2\sigma^2 + 4\Omega^2$, $\langle S_1^z \rangle = -\langle S_2^z \rangle = \sigma$ and $\tilde{J}_{ij} = (2J_{ij} + K_{ij})\frac{2\bar{V}_{ik}^2 \omega_k^2}{\tilde{\tilde{\omega}}_k^2}$

Equation (5) shows that the transition or Curie's temperature (T_c) is explicit function of the tunneling factor and the third and fourth-order phonon anharmonic interactions via $\tilde{J}_{ij}$ function.

Now from

$$\varepsilon = 1 + 4\pi\left\{-\lim_{x\to 0} 2\pi N\mu^2 G_{ij}(\omega + ix)\right\} \quad (6)$$

Dielectric Constant is obtained as

$$\varepsilon = -\frac{8\pi N\mu^2 \Omega\langle S_1^x \rangle}{\left(\omega^2 - \hat{\Omega}^2\right)} \quad (7)$$

Ratio of imaginary to real parts of dielectric constant is loss of tangent, i.e.

$$\tan\delta = \frac{imaginary \quad \varepsilon}{\mathrm{Re}\, al \quad \varepsilon} = -\frac{2\Omega\Gamma(\omega)}{\left(\omega^2 - \hat{\Omega}^2\right)} \quad (8)$$

Results and Discussion

By using the model values of a variety of physical quantities which appear in the evaluated expressions, thermal dependence of soft mode frequency, dielectric constant and loss tangent for different temperatures have been calculated and shown in figures 1,2 and 3. Model parameters for TGSe crystal used in present paper are given below.

T_c (K)	C (k)	Ω (cm^{-1})	J (cm^{-1})	K (cm^{-1})	V_{ik} (cm^{-1})	A_k	$N\times10^{-21}$ (cm^{-3})	$\mu\times10^{18}$ esu	ω_k (cm^{-1})
295.5	4727	0.2	320	160	0.01	10.2	3.81	3.43	6.2

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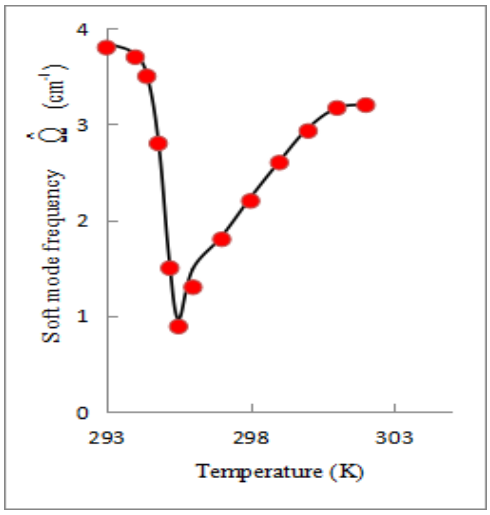

Fig 1. Thermal dependence of soft mode frequency of TGSe crystal (–our results, ● experimentally correlated vales for dielectric data)

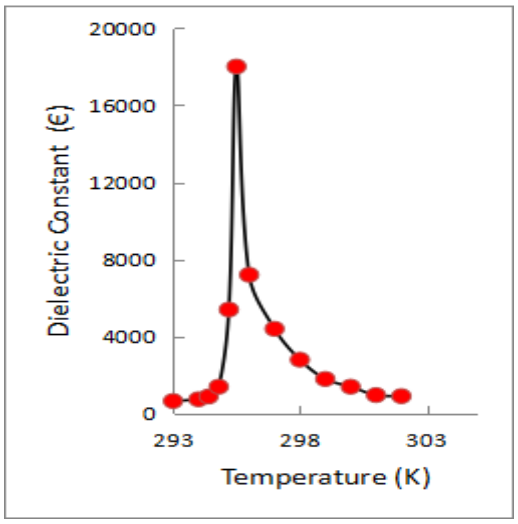

Fig 2. Thermal dependence of dielectric constant of TGSe crystal (–our results, ● experimentally values for dielectric data)

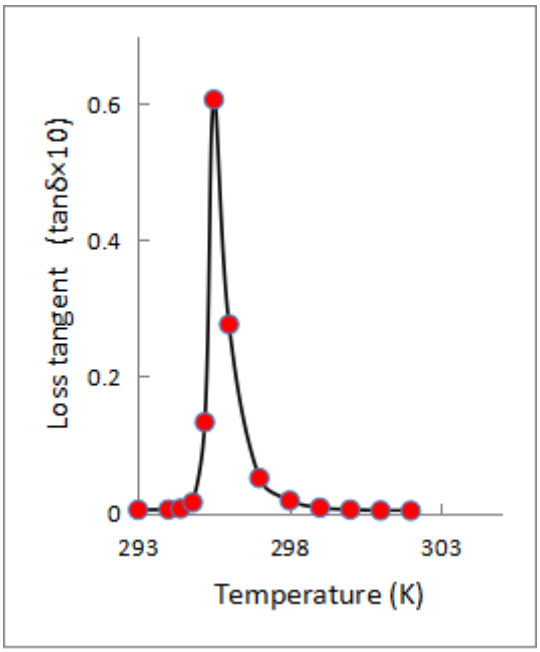

Fig 3. Thermal dependence of tangent loss of TGSe crystal (–our results, ● experimentally correlated vales for dielectric data)

From fig 1 which is the outcome of expression (3) evaluated in section 2, it is clear that soft mode frequency decreases as we approach from low temperature towards Curie temperature. At Curie temperature it becomes infinitesimally small and further increase in temperature leads to increase in soft mode frequency.

Similarly from fig 2 (outcome of expression (7)) and fig 3 (outcome of expression (8)) it is clear that the dielectric constant and tangent loss first increases as temperature increases. They become enormously large at transition temperature, further increase in temperature leads to decrease in their values. Our findings agree with experimental results of Polandov and Mylov et. al. (1968).

Earlier researchers [Chaudhuri and Choudhury et. al. 1988] have not considered phonon anharmonic interactions and also some spin-lattice interactions. Correlations are decoupled by them in an early stage. Due to this some significant interactions vanished from their calculations. If we neglect these corrections our results reduces to the results of Chaudhuri and Choudhury et. al. (1988). Theses corrections give better understanding and more precise results.

Conclusion

It can be concluded from above discussion that modification of PLCM model by introducing third and fourth order phonon anharmonic interactions and extra spin-lattice coupling terms assist explanation of phase transition and dielectric behaviour of TGSe crystal. Theoretical results are in agreement with experimental results witnessed the applicability of the present modified model for TGSe crystal.

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