DOI:10.7598/cst2016.1177
ISSN:2278-3458

Chemical Science Transactions
2016, **5(2),** 291-294

RESEARCH ARTICLE

Temperature Dependence of Ferroelectric Mode of Frequency, Dielectric Constant and Loss Tangent in Deuterated Triglycine Sulphate

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Received 20 November 2015 / Accepted 10 December 2015

Abstract: The model values of physical properties for deuterated triglycine sulphate crystal in theoretically derived expressions for FE mode frequency, dielectric constant and loss tangent in dependence of these quantities have been calculated and compared with experimental data of literature value. A good agreement is found.

Keywords: Ferroelectrics, Anharmonics, Dielectric, Loss tangent, Phase transition, Isotope effect

Introduction

Triglycine sulphate $NH_2CH_2(COO)_3H_2SO_4$(TGS) undergoes ferroelectric transition at 49 ^oC. On deuteration, the transition temperature shifts to 60 ^oC, showing large isotope effect. This fact suggests that hydrogen bond plays an important role in phase transition mechanism. The ferroelectric structure is monoclinic with space group $P2_1/m$ and the lattice dimensions are a = 9.15Å, b = 12.69 Å, c = Å, β = 105.4^o. This is low temperature phase. The paraelectric phase is monoclinic with space group 14/m.

Extensive experimental studies on TGS crystal and its deuterated form (DTGS) have been carried out by many experimentalists. Batra and Lal[1] have done crystal growth study. Electrical and mechanical properties have been studied by Murludharan *et al.,*[2]. Dielectric measurements were carried out on TGS and DTGS by Alexandru *et al.,*[3]. Vibrational spectral studies of pure and doped DTGS crystal were done by Arun *et al*[4]. Zolfagharien and Dizazi[5] have made growth and characterization study of DTGS. Prasalov *et al*.,[6] have done hysteresis study of DTGS crystal. Khanum and Podder[7] have done crystallization and characterization of TGS crystal doped with $NiSO_4$. Shreekumar and Philip[8] have done ultrasonic study of DTGS crystal. Aravazhi *et al*.,[9] have done dielectric and loss tangent measurements on DTGS crystal. Theoretical studies on TGS crystal were initiated by Blinc *et al*.,[10] who used Ising model. Chaudhuri *et al*.,[11] have considered a two-sub lattice pseudo spin model. They used Green's function method and

obtained soft mode frequency, susceptibility, dielectric constant and transition temperature. These authors[11] have not considered order phonon anharmonic interaction. They have decoupled the correlation at any stage. So that they could not produce better and convincing results. In the earlier paper one of authors[12] they have considered phonon anharmonic interactions terms[13].

In the present study we shall fit model values of physical quantities in the expressions obtained in one of authors earlier paper[12] for deuterated TGS crystal. Temperature dependences of ferroelectric mode frequency, dielectric constant and loss tangents will be calculated for DTGS crystal. Theoretical results will be compared with experimental results of Aravazhi *et al*[9].

Calculation and Results

In our earlier paper a two-sub lattice pseudo spin lattice coupled mode model along with third and fourth order phonon anharmonic interactions terms has been considered for TGS crystal. The Green's function is differentiated twice with respect to time t and t' with the help of modified Hamiltonian which is then set into Dyson's equation form. As a result Green's function was obtained as;

$$G(\omega) = \pi^{-1}\Omega\left\langle S_{i1}^{x}\right\rangle\delta_{ij}\left[\left(\omega^2 - \hat{\Omega}^2\right) + 2i\Omega\Gamma(\omega)\right]^{-1}, \tag{1}$$

where $\hat{\Omega}^2 = \tilde{\Omega}^2 + \Delta(\omega)$, (2)

$$\tilde{\Omega}^2 = a^2 + b^2 - bc \tag{3}$$

$$a = 2J_0\left\langle S_1^z\right\rangle + K_0\left\langle S_2^z\right\rangle, \tag{5}$$

$$b = 2\Omega \tag{6}$$

$$c = 2J_0\left\langle S_1^z\right\rangle + K_0\left\langle S_2^x\right\rangle \tag{7}$$

$\Delta(\omega)$ and $\Gamma(\omega)$ are shifts and width of response function of Green's function $G(\omega)$. Expression of $\Delta(\omega)$ and $\Gamma(\omega)$ have been given in our earlier paper[12]. Solving Eq (2) the FE mode frequency was obtained as;

$$\hat{\Omega}^2 = \frac{1}{2}\left\{\left(\tilde{\tilde{\omega}}_k^2 + \tilde{\tilde{\Omega}}\right) \pm \left[\left(\tilde{\tilde{\omega}}_k^2 - \tilde{\Omega}^2\right)^2 + 16V_{ik}\left\langle S_1^x\right\rangle\Omega\right]\right\}. \tag{7}$$

The dielectric constant ε is related to susceptibility χ as $\varepsilon = 4\pi\chi$ which in turn related[18] to retarded Green's function (2) as $\chi = -2N\mu^2 G(\omega + iX)$. Therefore putting value of Green's function (1) we have obtained value of dielectric constant ε as;

$$\varepsilon = \left(-8\pi N\mu^2\right)\left\langle S^x\right\rangle\left(\omega^2 - \tilde{\Omega}\right)\left[\left(\omega^2 - \hat{\Omega}\right)^2 + 4\Omega^2\Gamma^2\right]^{-1}. \tag{8}$$

The dissipation of power when crystal is exposed to electromagnetic field is expressed as loss tangent. The loss tangent is the ratio of imaginary to real parts of dielectric constant,

$$\tan\delta = \frac{2\Omega\Gamma(\omega)}{\hat{\Omega}^2} \tag{9}$$

By using model values of physical quantities for deuterated TGS crystal given in Table 1, temperature dependence of ferroelectric mode frequency, dielectric constant and loss tangent have been calculated and plotted in graph (Figures 1-3). Calculated temperature dependences have been compared with experimental values of Aravazhi *et al.,*[9].

Table 1. Model values of physical quantities of deuterated TGS crystal

T_c, ^oC	Ω cm^{-1}	J_0 cm^{-1}	$\bar{\upsilon}$ cm^{-1}	ω_k cm^{-1}	A_k cm^{-1}	C, ^oC	Nμ, $\mu C/cm^2$
60.70	0.01	470	15	1.92	14.22	4600	2.30 (at 30.70 ^oC)

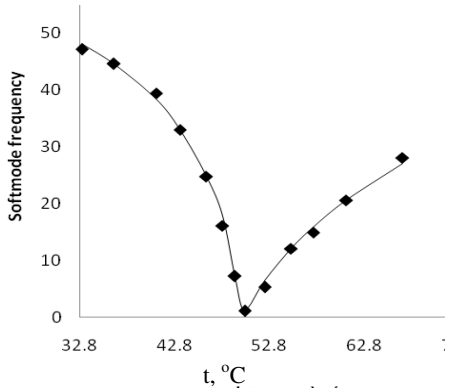

Figure 1. Calculated temperature dependence of soft mode frequency of DTGS crystal–, correlated Exp[9] values ♦

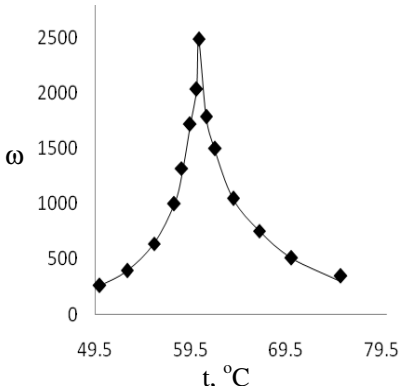

Figure 2. Calculated temperature dependence of dielectric constant in DTGS crystal–, Exp[9] ♦

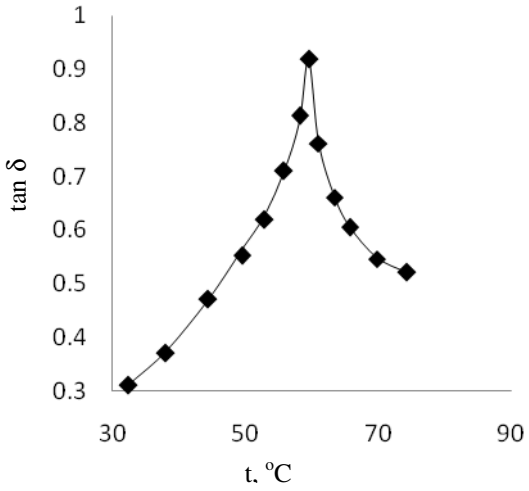

Figure 3. Calculated temperature dependence of loss tangent in DTGS crystal– Exp[9] ♦

Discussion

In the present work the temperature dependences of ferroelectric frequency, dielectric constant and loss tangent have been calculated. Theoretically calculated results compare with experimentally reported results of Aravazhi *et al*., for deuterated TGS very well.

The main aim of the present work is to explain isotope effect in DTGS crystal. On deuteration, the transition temperature shifts from 49^0 to $60\ ^0$C and both dielectric constant and loss tangent *versus* temperature curves shift from to new values. Our expression for transition temperature T_c with value for DTGS explains small isotope effect on T_c. Our expression (8), (9) and (10) explain the temperature dependences of ferroelectric mode frequency, dielectric constant and loss tangent for DTGS crystal. The Change in tunneling frequency is mainly responsible for isotope effect in DTGS crystal. Hence with the expressions obtained for DTGS crystal with different values of physical quantities, for DTGS Crystal, one can explain ferroelectric and isotope effect in deuterated TGS crystal.

Conclusion

Present study reveals that the two sub lattice pseudo spin-lattice coupled mode mode model along with third and fourth order phonon anharmonic interactions terms explain well the ferroelectric and dielectric behaviors of deuterated TGS crystal. Theoretical results agree with experimental results of Aravazhi *et al.,*[9] which shows the applicability of the present model.

Acknowledgement

Authors are grateful to Eminent Physicist Prof B S Semwal (Former Head) for his encouragement and to Prof Vinay Gupta (Delhi Univ.), Prof U C Naithani, Prof S C Bhatt and Dr Manish Uniyal for their encouragements. They are thankful to Dr Sandeep Sharma and Dr Ashish Nautiyal for the Discussions.

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