

Dielectric constant and Dielectric loss tangent for Rochelle Salt ferroelectric crystal

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Abstract: The Expression for dielectric susceptibility, dielectric constant, Curie-Weiss constant and dielectric loss tangent for Rochelle Salt ferroelectric crystal calculated by using Green Function the dielectric susceptibility, dielectric constant, Curie-Weiss constant and dielectric loss tangent have been calculated for different temperatures for ferroelectric Rochelle Salt crystal. With the help of these values the values of dielectric constant and loss tangent for Rochelle Salt crystal for different temperatures have been calculated. The calculated values of dielectric constant and loss tangent for Rochelle salt crystal have been shown in Tables and in figures. The values obtained have been compared with experimental values of Habltzul¹⁵ and Sandy & Jones⁵. Chaudhuri et al's⁷ calculated values have also been compared.

Keywords: Dielectric Susceptibility, Dielectric Constant, Curie-Weiss Constant, Dielectric Loss Tangent

I. Introduction

Ferroelectric crystals show anomalous dielectric behaviour, i.e., very high dielectric permittivity at phase transition temperature following a Curie-Weiss behaviour in paraelectric phase. The dielectric properties near transition temperature in ferroelectric crystals aroused a great deal of interest in the past to understand the inter-and intra-molecular interactions. The same information, in principle can be derived indirectly from acoustical methods because these crystals are piezoelectric (i.e., there is a bilinear coupling term involving the elastic strain and electronic polarisation).

The temperature and frequency dependences of dielectric susceptibility in ferroelectric Rochelle Salt crystal have been studied by many authors ever since Joseph Valasek¹ discovered ferroelectric properties of this crystal. Muller² has explained dielectric properties of Rochelle Salt by proposing his dipole theory. Mason³ explained the dielectric properties of Rochelle Salt using order-disorder model. Mitsui⁴ proposed a more realistic two-sublattice pseudospin model in contrast to Mason's single lattice model. Sandy and Jones⁵ have used Mitsui's formulae to explain their data of temperature dependence of dielectric constant in Rochelle Salt crystal. Konsin⁶ has used pseudospin model with proton-phonon interaction and asymmetrical hydrogen bond to explain spontaneous polarization and dielectric constant in Rochelle Salt. Chaudhuri et al⁷ have used a two sublattice pseudospin-lattice coupled mode model with a fourth-order anharmonic phonon interaction term to study dielectric properties of ferroelectric Rochelle Salt crystal. Some good results have been obtained. Recently Satsyuk and Velychko⁸ have proposed a four-sublattice model which is extension of Mitsui's two sublattice model to explain dielectric properties of Rochelle Salt. This model allows to investigate the temperature and field behaviours of transverse (besides longitudinal) components of dielectric susceptibility.

Experimental studies of dielectric properties of Rochelle Salt crystal have been made by Sandy and Jones⁵, Valasek⁹, Frayne¹⁰, Sawyer and Tower¹¹, Zeleny and Valasek¹², Sorokin and Posnov¹³, Bancraft¹⁴, Hablutzel¹⁵, Valasek¹⁶, Akao and Sasaki¹⁷, Riyujii¹⁸, Man Singh et al¹⁹, Fillipic et al²⁰, Kalisz et al²¹, Schneider et al²², Malyskina²³, Kikuta et al²⁴, Yaldovker et al²⁵ and Slivka et al²⁶. These authors measured the dielectric constant at different temperatures and frequencies in the vicinity of the phase transition points in ferroelectric Rochelle Salt crystal. These studies showed anomalous increase in the value of dielectric constant and dielectric loss at both transition points in Rochelle Salt.

Muller's theoretical work was interaction mechanism. Mason's work was interaction mechanism. Mason's work was Lorentz field theory based on order-disorder of dipole in asymmetrical potentials. However, Mitsui's two-sublattice model theory was semi-phenomenological. They attempted to explain ferroelectric phase transition in Rochelle Salt. But they could not produce a comprehensive explanation and fit to experimental facts. Chaudhuri et al⁷ have considered phonon anharmonic interaction term also to study dielectric properties of Rochelle Salt type crystal, but even not in a convincing way. They truncated the correlations in an early stage and so could not obtain shift and width in the pseudospin frequency response, which are consequences of all possible interactions in a real crystal. They could not explain dielectric tangent loss, which is an attractive and important property of all ferroelectric crystals. According to Cochran²⁸, in ferroelectric crystals, the frequency of some of relevant normal modes of vibration decreases on approaching transition temperature and becomes zero at it. This mode called soft mode is responsible for phase transition or

ferroelectric to paraelectric phase and from low symmetry to high symmetry crystal structure. It is this mode which largely determines the dielectric properties of ferroelectric crystals.

In the present paper, the expression for dielectric constant and dielectric loss tangent have been obtained for Rochelle Salt ferroelectric crystal directly with the help of shift, width and the renormalized soft mode frequency. The double-time temperature dependent Green's function technique²⁹ and Dyson's equation treatment have been used for the evaluation. The two-sublattice pseudospin model⁷ with third-and fourth-order phonon anharmonic interaction terms^{30, 31} has been used in the calculation. By using model values of physical quantities from literature, the temperature dependences of dielectric constant and loss tangent near phase transition temperature have been calculated for Rochelle salt crystal. The calculated theoretical results have been compared with experimental results of, Hablutzel¹⁵ and Sandy Jones⁵.

II. Theory

General Formulation

The dielectric constant is the ratio of the forces between charges in a vacuum to the forces between the same charges, at the same distance apart, in the dielectric.

The response of a crystal to an external electric field is conveniently described by the dielectric susceptibility. Following Zubarev³⁰, the general expression for complex dielectric susceptibility tensor $\chi_{\mu\nu}(\omega)$ can be expressed as

$$\chi_{\mu\nu}(\omega) = \lim_{x \rightarrow \infty} -2\pi N \mu^2 G_{\mu\nu}(\omega + ix), \quad (1)$$

where $G_{\mu\nu}(\omega)$ is the Fourier transform of the retarded double-time temperature dependent Greens' function between μ^{th} and ν^{th} components of the crystal dipole moment operator $\vec{M}(\omega)$ in the Heisenberg representation and is defined as

$$\begin{aligned} G_{\mu\nu}(t - t') &= \langle\langle M_{\mu}(t); M_{\nu}(t') \rangle\rangle \\ &= -i\theta(t - t') \langle [M_{\mu}(t); M_{\nu}(t')] \rangle, \end{aligned} \quad (2)$$

where $\theta(t - t')$ is the Heaviside's unit step function and the angular bracket $\langle \dots \rangle$ denotes the thermal ensemble average.

The crystal dipole moment \vec{M} depends on the ionic coordinates, like the potential energy, i.e., on the lattice configuration and can be expanded in a Taylor series in terms of ionic displacements. Because of the cyclic boundary conditions, i.e., symmetry considerations, imposed on the ionic motion, only the soft optical mode has a non-zero polarization associated with it. Thus only the expansion coefficients which correspond to

lowest frequency optic mode, i.e., $\vec{M}(\omega)$ contributes to the dielectric susceptibility, Therefore, one considers only one transverse optic branch which is possible in the ferroelectric crystal in the paraelectric phase. Therefore, the ferroelectric crystals having cubic symmetry in the paraelectric phase, the scalar susceptibility $\chi(\omega) = -\chi_{\mu\mu}$ can be expressed as

$$\chi = \lim_{X \rightarrow 0} -2\pi N \mu^2 G_{ij}(\omega + iX) \quad (3)$$

where, N is the number of unit cells in the sample and μ is the effective dipole moment per unit cell. The Green's function $G_{ij}(\omega + iX)$ is given by

$$\begin{aligned} G_{ij}(\omega + iX) &= \langle\langle S_{1i}^z(t); S_{1j}^z(t') \rangle\rangle_{(\omega+iX)} \\ &= G'_{ij}(\omega) - iG''_{ij}(\omega). \end{aligned} \quad (4)$$

Here $G'_{ij}(\omega)$ and $G''_{ij}(\omega)$ are real and imaginary parts respectively of the Green's function as has been evaluated.

The dielectric constant $\epsilon(\omega)$ can be evaluated using the relation

$$\begin{aligned} \epsilon(\omega) &= 1 + 4\pi\chi \\ &= \epsilon'(\omega) - i\epsilon''(\omega), \end{aligned} \quad (5)$$

where $\epsilon'(\omega)$ and $\epsilon''(\omega)$ are real and imaginary parts of the dielectric constant ϵ . In ferroelectric crystals $\epsilon(\omega) \gg 1$.

The real part of the dielectric constant, ϵ' , can be expressed as

$$\epsilon'(\omega) = -8\pi N\mu^2 G'_{ij}(\omega) \quad (6a)$$

and the imaginary part ϵ'' as

$$\epsilon''(\omega) = -8\pi N\mu^2 G''_{ij}(\omega), \quad (6b)$$

where $G'_{ij}(\omega)$ and $G''_{ij}(\omega)$ are real and imaginary part of Green's function.

In any dielectric material there will be some power loss because of the work done to overcome the frictional damping forces encountered by the dipoles during their rotation. If an a.c. field is considered, then in an ideal case the charging current I_c will also be produced, which is in phase with the voltage. Charging current I_c and loss current I_L will be 90° out of phase with the voltage. But in most of the capacitors, due to the absorption of electrical energy some loss current, I_L will make angles δ and θ , respectively with the total current, I passing through the capacitor. The loss current is represented by $\sin \delta$ of the total current, I . Generally, $\sin \delta$ is called the loss factor but when δ is small then $\sin \delta = \delta = \tan \delta$. But the two components ϵ' and ϵ'' of the complex dielectric constant, ϵ , will be frequency dependent and are given as

$$\epsilon'(\omega) = D_o \cos \delta / E_0, \quad (7)$$

$$\epsilon''(\omega) = D_o \sin \delta / E_0. \quad (8)$$

Since the displacement vector in a time varying field will not be in phase with E and hence there will be a phase difference δ between them. From Eqs. (7) and (8) one gets

$$\tan \delta = \frac{\epsilon''(\omega)}{\epsilon'(\omega)}. \quad (9)$$

Therefore, the evaluation of dielectric constant (ϵ) and loss tangent ($\tan \delta$) involves the evaluation of retarded double-time thermal Green's function defined and evaluated.

III. Dielectric Constant

Substituting the value of Green's function in Eq. (6a), one obtains real part of dielectric constant ϵ' as

$$\epsilon'(\omega) = - \frac{8\pi N\mu^2 \Omega \langle S_i^x \rangle (\omega^2 - \hat{\Omega}_-^2)}{\left[(\omega^2 - \hat{\Omega}_-^2)^2 + 4\Omega^2 \Gamma^2(\omega) \right]}, \quad (10)$$

and the imaginary part ϵ'' as

$$\epsilon''(\omega) = - \frac{8\pi N\mu^2 \Omega \langle S_i^z \rangle 2\Omega \Gamma(\omega)}{\left[(\omega^2 - \hat{\Omega}_-^2)^2 + 4\Omega^2 \Gamma^2(\omega) \right]}. \quad (11)$$

Expanding Eqs. (10) near phase transition point, one gets

$$\epsilon(\omega) = \frac{C}{(T - T_c)}, \quad (12)$$

where

$$C = \frac{8N\mu^2 \tanh\left(\frac{\Omega}{k_B T_c}\right) k_B T_c^2}{\Omega \tilde{J}_q \left(1 - \tanh^2 \frac{\Omega}{2k_B T_c}\right)} \quad (13)$$

is the Curie-Weiss constant. The expression (12) is the well known Curie-Weiss law.

IV. Dielectric Loss Tangent

Substituting Eqs. (10) and (11) into Eq. (9), the expression for the dielectric loss (tangent loss) is obtained as

$$\tan \delta = -\frac{2\Omega\Gamma(\omega)}{(\omega^2 - \hat{\Omega}^2)}. \quad (14)$$

At microwave frequencies, $\omega, (\hat{\Omega} \gg \omega)$ so that Eq. (14) gets reduced to

$$\tan \delta = \frac{2\Omega\Gamma(\omega)}{\hat{\Omega}^2}. \quad (15)$$

In view of the temperature dependence of the square of soft mode frequency, $\hat{\Omega}^2 = K(T - T_c)$ and temperature dependence of the width, $\Gamma(\omega)$, the temperature dependence of the dielectric loss tangent in the paraelectric phase is obtained as a polynomial equation

$$(T - T_c) \tan \delta = (A + BT + CT^2), \quad (16)$$

where A, B and C are constants, which depend upon crystal defects, third-order and fourth-order phonon anharmonic interactions respectively. For pure single crystal, the first term on right hand side vanishes, while the second and third terms are intrinsic property of the crystal.

V. Numerical Calculation of Dielectric Constant and Loss Tangent

The quantities $\langle S_1^z \rangle, \langle S_2^z \rangle, \tilde{\Omega}, \tilde{\tilde{\Omega}}, \hat{\Omega}, \Delta_s, \Gamma_s, \Delta_{s-p}(\omega)$ and $\Gamma_{s-p}(\omega)$ etc. have been calculated for different temperatures for ferroelectric Rochelle Salt crystal. With the help of these values from Eqs. 10) and (15), the values of dielectric constant (ϵ) and loss tangent ($\tan \delta$) for Rochelle Salt crystal for different temperatures have been calculated. The calculated values of dielectric constant (ϵ) and loss ($\tan \delta$) for Rochelle Salt crystal have been shown in Table (1) and Table (2) and in fig. 1 and 2. The values obtained have been compared with experimental values of Habltzul¹⁵ and Sandy & Jones⁵. Chaudhuri et al's⁷ calculated values have also been compared.

Table 1 Calculated values of Dielectric constant (ϵ) for Rochelle Salt crystal.

Temperature (K)	ϵ
240	14.7906827675
245	29.5977187282
250	44.5191269141
255	3371.0151967310
260	1836.62342
265	1528.2680
270	1541.1850266132
275	1658.9696083570
280	1778.5644516823

285	1897.4652929107
290	2022.0078978758
295	1754.8265
297	2080.8258805072
300	1403.8006345139
305	1083.3084477409
310	150.2151203980
315	60.3093099704
320	45.1376375634
325	30.0095852977
330	14.9832986788

Table 2 Calculated values of loss tangent ($\tan \delta$) for Rochelle Salt crystal.

Temperature (K)	$\tan \delta$
240	0.313953
245	0.3142
250	0.31657
255	0.624808
260	0.296803
265	0.313874
270	0.295833
275	0.325901
280	0.313741
285	0.316407
290	0.323573
295	0.342428
297	0.594073
300	0.362204
305	0.352276
310	0.321152
315	0.319237
320	0.318606
325	0.317903
330	0.317353

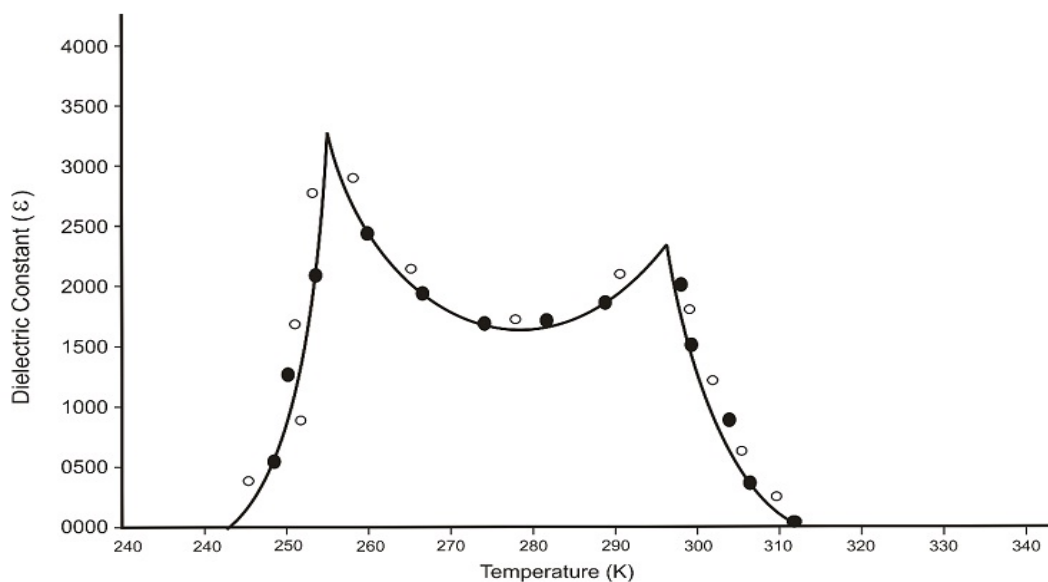


Fig. 1 Temperature dependence of ϵ in Rochelle Salt crystal
[- Present calculation, ● Experimental data of Habtzul¹⁵, ○ Calculation of Chaudhuri et al⁷.]

Figure 1. Calculated values of Dielectric constant for Rochelle Salt crystal.

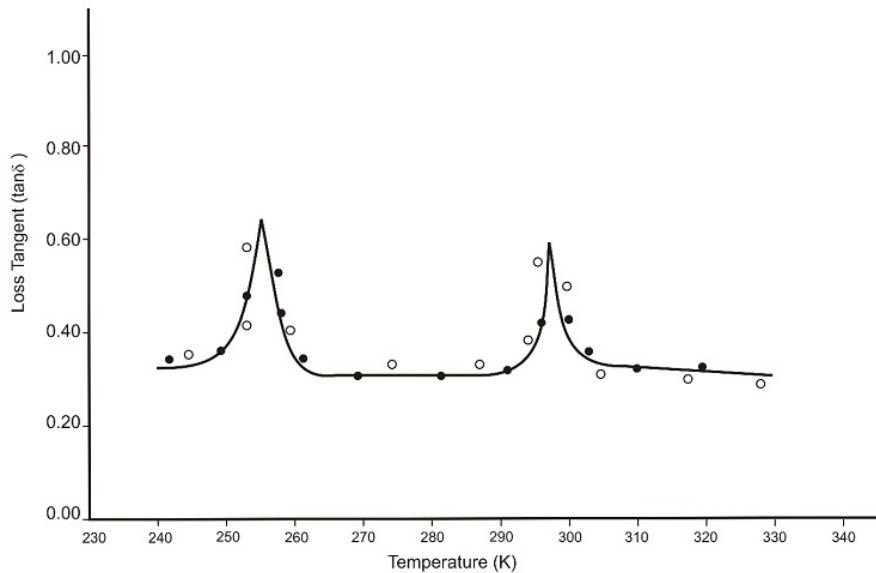


Fig. 2 Temperature dependence of $\tan\delta$ in Rochelle Salt crystal
 [- Present calculation, • Experimental data of Habltzul¹⁵, ○ Calculation of Chaudhuri et al⁷.]
Figure 2. Calculated values of loss tangent ($\tan \delta$) for Rochelle Salt crystal.

It is observed from tables (1) and (2) and figures 1 and 2 that the dielectric constant steeply increases from low temperature 240K towards first transition temperature 255K then decreases upto 273K and again increases upto second transition temperature 297K. After second transition temperature it again decreases. Above transition temperature the dielectric constant decreases with increase in temperature. Similarly, the dielectric loss first increases from low temperature (240K) upto first transition temperature (255K). Above transition temperature the dielectric (tangent) loss decreases upto 275K and again increases upto 297K, after 297K it is again decreases. It shows anomalous behaviour, near both transition, temperatures 255K and 297K.

It is observed that our theoretical results for temperature dependence of ϵ and $\tan \delta$ compare well with experimentally reported results of, Sandy & Jones⁵ and Habltzul¹⁵.

It the width, shift and third-order phonon interaction is neglected from our calculations, our expressions reduce to the expressions obtained by Chaudhuri et al⁷. Now, using expressions of our study with some little changes and model parameters which are different for other similar crystal like PbHPO_4 , TGS, $\text{C}_4\text{O}_4\text{H}_4$, and their deuterated forms similarly temperature variations of dielectric constant and loss tangent can be easily obtained for these crystals. Therefore, it can be said that the two-sublattice pseudospin-lattice coupled mode model along with third- and fourth-order phonon anharmonic interaction terms explains well the dielectric properties of ferroelectric Rochelle Salt crystal.

VI. Conclusion

By using double-time temperature dependent Green's function method and the Dyson's equation treatment in the two sublattice pseudospin-lattice coupled mode model Hamiltonian considering third-and fourth-order phonon anharmonic interaction terms for lead hydrogen phosphate type ferroelectric crystals. With the help of already evaluated Green's function the expression for dielectric constant and dielectric (tangent) loss have been evaluated. Eqs. (10) and (15) of present calculations show that the dielectric constant (ϵ) and loss ($\tan \delta$) depend on phonon anharmonic interactions. Since both of these quantities are functions of renormalized soft mode frequency ($\hat{\Omega}$) and the width $\Gamma(\omega)$ which are clearly seen to be explicit functions

of phonon anharmonic interaction. In the classical limit of high temperature $n_k = \coth\left(\frac{\tilde{\omega}_k}{2kT}\right)$ reduces to

$\left(\frac{\tilde{\omega}_k}{2kT}\right)$ i.e., $n_k = \left(\frac{2kT}{\tilde{\omega}_k}\right)$. Therefore, phonon occupation numbers n_k 's become large. The dielectric loss

corresponds to the width associated with damping of soft mode (see Eq. 15). The damping of the soft mode can be understood as the creation of a virtual polarization mode excited by the transverse electromagnetic radiation and subsequent decay into real phonons by scattering from third-and fourth-order phonon anharmonic

interaction. At higher a temperature, the loss deviates from the Curie-Weiss type behaviour and increases linearly with temperature. This behaviour assumes that at higher temperatures the phonon anharmonic interaction is responsible for the observed loss. The values of dielectric loss increases and shows two maximas at two transitions (255K and 297K). Between the two transitions the loss remains high through much less as compared to that near transition points. The loss decreases when the temperature is lowered below first transition temperature (255K) because this reduces the domain mobility. The loss near the Curie temperature increases due to high domain mobility. An analytic expression for frequency and temperature dependences of dielectric tangent loss of a ferroelectric crystal can be obtained by considering the dynamics of the domain wall motion.

By using present expressions, and model values for deuterated Rochelle salt crystal, similarly variations of dielectric constant and loss can be obtained for deuterated Rochelle Salt crystal. The two-sublattice pseudospin-lattice coupled mode model along with third-and fourth-order phonon anharmonic interaction terms is found suitable to explain the dielectric properties of ferroelectric Rochelle salt crystal.

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