

Electric field dependent microwave losses in $Ba_xSr_{1-x}TiO_3$ perovskites

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The electric field dependent microwave loss of anharmonic $Ba_xSr_{1-x}TiO_3$ perovskites has been calculated in its para electric phase from the Silverman Joseph Hamiltonian augmented with fourth order phonon co-ordinates using double time Greens functions. The results are used to obtain an expression for the frequency and temperature dependence of dielectric loss at microwave frequencies due to impurity and anharmonic scattering. The loss tangent consists of a contribution which is quadratic in applied biasing and field independent. The variation of $\tan\delta$ with applied field is noticeable in the vicinity of Curie temperature. In the higher temperature region, the electric field effect ceases and the increase in loss arises mainly due to higher order anharmonic terms.

Keywords: Anharmonicity, Softmode, Microwave loss tangent, Displacive ferroelectrics

1 Introduction

There has been considerable interest in the physical properties of mixed crystals, as they find interesting applications and their study helps in understanding basic mechanism of mixed crystal formation. Dependence of physical properties of mixed crystals varies from system to system. The property may change in a linear or non-linear manner. For example solid solution of $BaTiO_3$ with other ferroelectrics of same class and also with certain compounds, which are not themselves ferroelectric, possess ferroelectric properties and change in the composition of the solid solution makes it possible to regulate the Curie point within broad range of temperature. Among all these perovskites of mixed systems $Ba_xSr_{1-x}TiO_3$ has been identified as the leading material for under cooled detector fabrication¹, photo refractive mirrors²⁻³ and as a gate insulator of the oxide super conductors FET in the thin film.⁴

Microwave loss in the mixed and pure $SrTiO_3$ ceramics as a function of temperature and frequency has been experimentally measured earlier. Experimental and theoretical studies on $Ba_xSr_{1-x}TiO_3$ have been done by many workers⁵⁻¹⁴.

The investigation of dielectric properties provides an important approach in understanding intra and intermolecular interactions modes of the motion and conformational change in the macromolecules. The temperature, defect and frequency dependence of the dielectric loss in ferroelectric perovskites has been the subject of considerable interest due to their

extensive use in optical communication, memory display, temperature control devices and ceramic industry.

Microwave loss obeys the Curie–Wiess law. This may be taken as a direct evidence for the temperature dependence of the polarization mode frequency. At transition temperature, the soft mode frequency tends to zero and lattice displacement associated with this mode becomes unstable. This explains the anomalous behaviour of the dielectric loss near the phase transition. It is now clear on theoretical grounds that absorption of a microwave cannot be due to absorption or creation of single phonons. Energy and momentum cannot be simultaneously conserved in the process, since the momentum of the microwave photons is negligible compared to that of an excited phonon. It is possible, however, to excite a virtual phonon with energy equal to that of a microwave photon, which subsequently decays into a real phonon due to interactions with lattice-imperfections. Imperfections simply play the role of absorbing the excess momentum of the phonons and decay into other vibrational modes of materials is also possible. Study on microwave loss tangent in pure and mixed ferroelectric perovskites is done by many workers.¹⁵⁻²³ Microwave loss in $Ba_xSr_{1-x}TiO_3$ perovskites has been discussed earlier²⁴.

In the present work variation of microwave loss tangent ($\tan\delta$) with frequency and temperature in presence of applied external electric field in $Ba_xSr_{1-x}TiO_3$ perovskites has been discussed. It has

been taken into consideration that the Curie temperature T_c of Ba_xSr_{1-x}TiO₃ is displaced to higher temperature by application of biasing field.

2 Theory

For quantitative purpose the Curie temperature changes with electric field is as follows:²⁵

$$\Delta T_c = 1.9 \times 10^{-3} \times E \quad \dots (1)$$

where E is measured in volt/cm.

Above the phase transition the temperature dependence of loss tangent is well represented by

$$(T - T_c) \tan \delta = \omega(\alpha + \beta T + \gamma T^2). \quad \dots (2)$$

Here T_c is Curie temperature and the parameter α is shown to be determined by lattice imperfection and vanishes for pure single crystalline material. The parameters β and γ , which are related to third and fourth order anharmonic terms in the interionic potential respectively are shown to be intrinsic properties of perfect lattice and are modified in presence of an electric field.

2.1 Hamiltonian and Green's functions

The Hamiltonian, which includes the anharmonicity up to fourth order in the potential energy due to interactions of the soft mode coordinates, resonant interaction and scattering terms is considered. The impurities introduced are characterized by a different mass than the host atoms and with modified nearest neighbour harmonic force constants around their sites. Their influence on the anharmonic coupling co-efficient in the Hamiltonian is neglected.

For deriving an expression for the response function and hence for the dielectric loss we use the modified Silverman-Joseph Hamiltonian for the doped displacive ferroelectrics in the presence of external electric field. Double time thermal Greens function technique is used to obtain thermally averaged correlation function and hence the observable quantities with the help of the modified model Hamiltonian. The Hamiltonian used in the present study is exactly similar to previous study and the notations used are the same and also in the same sense¹³. Recently this Hamiltonian is used in obtaining an expression for field dependent dielectric constant¹¹ of Ba_xSr_{1-x}TiO₃.

For the study of loss tangent the following Green's function is used.

$$G_0^0(\omega + i\epsilon) = \ll A_0^0(t); A_0^0(t') \gg_{\omega+i\epsilon} = G'(\omega) - iG''(\omega), \quad \dots (3)$$

which gives the real part of dielectric constant as

$$\epsilon'(\omega) - 1 = -8\pi^2 M_\mu^2(0) G'(\omega) \quad \dots (4)$$

and loss tangent

$$\tan \delta = G''(\omega) / G'(\omega) \quad \dots (5)$$

Writing the equation of motion for the Green's function (Eq. (3)) with the help of modified Hamiltonian, Fourier transforming and writing it in the Dysons equation, one obtains

$$G_0^0(\omega + i\epsilon) = \omega_0^0 / \pi [\omega^2 - \bar{\nu}_0^0(\omega) + i\bar{\Gamma}_0^0(\omega)], \quad \dots (6)$$

where $\bar{\nu}_0^0(\omega) =$

$$-(\omega_0^0)^2 + 4\omega_0^0 D(0,0) + \omega_0^0 E^2 (96g^2V - 24gD'_1) + 4\omega_0^0 \bar{Q} + \bar{\Delta}_0^0(\omega) \quad \dots (7)$$

Here $\bar{\Delta}_0^0(\omega)$ is defect, temperature and field dependent shift of soft mode frequency. $D(0,0)$ is defect dependent parameter depending upon harmonic force constant change. g and D'_1 are linear and second order electric moment coefficients respectively.

$$\begin{aligned} \bar{\Delta}_0^0(\omega) = & \text{Re} \omega_0^0 [2 \sum_k |F(k)|^2 \sum_{\pm} (\tilde{N}_k^0 \pm \tilde{N}_k^a) \\ & \frac{(\tilde{\omega}_k^a \pm \tilde{\omega}_k^0)}{\omega^2 - (\tilde{\omega}_k^a + \tilde{\omega}_k^0)^2} \\ & + 8 \sum_{k,\lambda} |\beta^\lambda(k)|^2 ([1 + (\tilde{N}_k^\lambda)^2 + 2\tilde{N}_0^0 \tilde{N}_k^\lambda] \\ & \frac{\Omega + 2\tilde{\omega}_k^\lambda}{\omega^2 - (\Omega + 2\tilde{\omega}_k^\lambda)^2} \\ & + [1 + (\tilde{N}_k^\lambda)^2 - 2\tilde{N}_0^0 \tilde{N}_k^\lambda] \frac{(\Omega - 2\tilde{\omega}_k^\lambda)}{\omega^2 - (\Omega - 2\tilde{\omega}_k^\lambda)^2} \\ & - [1 - (\tilde{N}_k^\lambda)^2] \frac{2\Omega}{\omega^2 - \Omega^2}) \end{aligned}$$

$$\begin{aligned}
 & + \sum_{k_1, k_2, k_3} \sum_{k_1', k_2', k_3'} \delta_{123} \Phi(k_1, k_2, k_3) \Phi(k_1', k_2', k_3') \\
 & \quad [1 + \tilde{N}_{k_1}^0 \tilde{N}_{k_2}^a + \tilde{N}_{k_2}^a \tilde{N}_{k_3}^a + \tilde{N}_{k_3}^a \tilde{N}_{k_1}^0] \\
 & \quad \frac{(\tilde{\omega}_{k_1}^0 + \tilde{\omega}_{k_2}^a + \tilde{\omega}_{k_3}^a)}{\omega^2 - (\tilde{\omega}_{k_1}^0 + \tilde{\omega}_{k_2}^a + \tilde{\omega}_{k_3}^a)^2} + \\
 & \quad [1 - \tilde{N}_{k_1}^0 \tilde{N}_{k_2}^a + \tilde{N}_{k_2}^a \tilde{N}_{k_3}^a - \tilde{N}_{k_3}^a \tilde{N}_{k_1}^0] \\
 & \quad \left. \frac{(\tilde{\omega}_{k_1}^0 - \tilde{\omega}_{k_2}^a - \tilde{\omega}_{k_3}^a)}{\omega^2 - (\tilde{\omega}_{k_1}^0 - \tilde{\omega}_{k_2}^a - \tilde{\omega}_{k_3}^a)^2} \right] \\
 & + \sum_{k_1, k_2, k_3} \sum_{k_1', k_2', k_3'} \delta \Psi(k_1, k_2, k_3) \psi(k_1', k_2', k_3') \\
 & \times [1 + \tilde{N}_{k_1}^0 \tilde{N}_{k_2}^0 + \tilde{N}_{k_2}^0 \tilde{N}_{k_3}^0 + \tilde{N}_{k_3}^0 \tilde{N}_{k_1}^0] \\
 & \quad \frac{(\tilde{\omega}_{k_1}^0 + \tilde{\omega}_{k_2}^0 + \tilde{\omega}_{k_3}^0)}{\omega^2 - (\tilde{\omega}_{k_1}^0 + \tilde{\omega}_{k_2}^0 + \tilde{\omega}_{k_3}^0)^2} \\
 & \quad [1 - \tilde{N}_{k_1}^0 \tilde{N}_{k_2}^0 + \tilde{N}_{k_2}^0 \tilde{N}_{k_3}^0 - \tilde{N}_{k_3}^0 \tilde{N}_{k_1}^0] \\
 & + \frac{(\tilde{\omega}_{k_1}^0 - \tilde{\omega}_{k_2}^0 - \tilde{\omega}_{k_3}^0)}{\omega^2 - (\tilde{\omega}_{k_1}^0 - \tilde{\omega}_{k_2}^0 - \tilde{\omega}_{k_3}^0)^2} \\
 & + 48 E^2 \left(\frac{\omega_{k_1}^0}{\omega^2 - \omega_{k_1}^0 \omega_{k_2}^0} \right) \\
 & \left[\sum_k D(k^0, 0) B^0(k) - 4g\beta^0(k) \right. \\
 & \times \sum_{k_1, k_2} \{D(k_1, k_2, -k) - 2g\Psi(k_1, k_2, -k)\} \times \sum_{\pm} (\tilde{N}_{k_1}^0 \pm \tilde{N}_{k_2}^0) \\
 & \times \frac{\tilde{\omega}_{k_1}^0 \pm \tilde{\omega}_{k_2}^0}{\omega^2 - (\tilde{\omega}_{k_1}^0 \pm \tilde{\omega}_{k_2}^0)^2}, \dots (7a)
 \end{aligned}$$

$$\text{where } \omega_{k_1}^0 = \omega_k^0 + 4 \sum_{k_1} C(k_1^0, -k) \dots (7b)$$

and

$$\begin{aligned}
 \omega_{k_2}^0 & = \omega_k^0 - 4 \sum_{k_1} D(k_1^0, -k) - 8E^2 [2g^2 \sum_k \beta^0(k) \\
 & \quad \square g \sum_k B^0(k)] \dots (7c)
 \end{aligned}$$

also $\bar{\Gamma}_0^0(\omega) =$

$$\begin{aligned}
 & \omega_0^0 \pi \left[\sum_k |F(k)|^2 \sum_{\pm} (\tilde{N}_k^0 \pm \tilde{N}_k^a) \{ \delta(\omega - \tilde{\omega}_k^a \mu \tilde{\omega}_k^0) \right. \\
 & \quad - \delta(\omega + \tilde{\omega}_k^a \pm \tilde{\omega}_k^0) \} + 4 \sum_{k, \lambda} |\beta^\lambda(k)|^2 ([1 + (\tilde{N}_k^\lambda)^2 + 2N_0^0 \tilde{N}_k^\lambda] \\
 & \quad \times \{ \delta(\omega - \Omega - 2\tilde{\omega}_k^\lambda) - \delta(\omega + \Omega + 2\tilde{\omega}_k^\lambda) \} \\
 & \quad + [1 + (2\tilde{N}_k^\lambda)^2 - 2N_0^0 2\tilde{N}_k^\lambda] \\
 & \quad \times \delta(\omega - \Omega + 2\tilde{\omega}_k^\lambda) - \delta(\omega + \Omega - 2\tilde{\omega}_k^\lambda) \} - [1 - (\tilde{N}_k^\lambda)^2] \\
 & \quad \times \delta(\omega - \Omega) - \delta(\omega + \Omega) \} \\
 & + \sum_{k_1, k_2, k_3} \sum_{k_1', k_2', k_3'} (1/2) \delta_{123} \Phi(k_1, k_2, k_3) \\
 & \times \Phi(k_1', k_2', k_3') ([1 + \tilde{N}_{k_1}^0 \tilde{N}_{k_2}^a + \tilde{N}_{k_2}^a \tilde{N}_{k_3}^a + \tilde{N}_{k_3}^a \tilde{N}_{k_1}^0] \\
 & \times \{ \delta(\omega - \tilde{\omega}_{k_1}^0 - \tilde{\omega}_{k_2}^a - \tilde{\omega}_{k_3}^a) - \delta(\tilde{\omega} + \tilde{\omega}_{k_1}^0 + \tilde{\omega}_{k_2}^a + \tilde{\omega}_{k_3}^a) \} \\
 & + [1 - \tilde{N}_{k_1}^0 \tilde{N}_{k_2}^a + \tilde{N}_{k_2}^a \tilde{N}_{k_3}^a - \tilde{N}_{k_3}^a \tilde{N}_{k_1}^0] \{ \delta(\omega - \tilde{\omega}_{k_1}^0 + \tilde{\omega}_{k_2}^a + \tilde{\omega}_{k_3}^a) \\
 & \quad - \delta(\omega + \tilde{\omega}_{k_1}^0 - \tilde{\omega}_{k_2}^a - \tilde{\omega}_{k_3}^a) \} \\
 & + (1/2) \sum_{k_1, k_2, k_3} \sum_{k_1', k_2', k_3'} \delta \Psi(k_1, k_2, k_3) \\
 & \times \psi(k_1', k_2', k_3') ([1 + \tilde{N}_{k_1}^0 \tilde{N}_{k_2}^0 \\
 & + \tilde{N}_{k_2}^0 \tilde{N}_{k_3}^0 + \tilde{N}_{k_3}^0 \tilde{N}_{k_1}^0] \{ \delta(\omega - \omega_{k_1}^0 \\
 & \quad - \tilde{\omega}_{k_2}^0 - \tilde{\omega}_{k_3}^0) - \delta(\omega + \tilde{\omega}_{k_1}^0 + \tilde{\omega}_{k_2}^0 + \tilde{\omega}_{k_3}^0) \} + [1 - \tilde{N}_{k_1}^0 \tilde{N}_{k_2}^0 \\
 & + \tilde{N}_{k_2}^0 \tilde{N}_{k_3}^0 - \tilde{N}_{k_3}^0 \tilde{N}_{k_1}^0] \delta(\omega - \tilde{\omega}_{k_1}^0 + \tilde{\omega}_{k_2}^a + \tilde{\omega}_{k_3}^a) - \delta(\omega + \tilde{\omega}_{k_1}^0 \\
 & \quad - \tilde{\omega}_{k_2}^a - \tilde{\omega}_{k_3}^a) \} + 2 \sum_{k, \lambda} D^2(k_\lambda, 0) \{ \delta(\omega - \tilde{\omega}_k^\lambda) - \delta(\omega + \tilde{\omega}_k^\lambda) \} \\
 & \quad - 2(\omega / \omega_0^0)^2 \\
 & \quad \sum_{k, \lambda} C^2(k_\lambda, 0) \{ \delta(\omega - \tilde{\omega}_k^\lambda) - \delta(\omega + \tilde{\omega}_k^\lambda) \} + 2(\omega / \omega_0^0) \\
 & \quad \times \sum_{k, \lambda} D^*(k_\lambda, 0) C(k_\lambda, 0) \{ \delta(\omega - \tilde{\omega}_k^\lambda) - \delta(\omega + \tilde{\omega}_k^\lambda) \} - 2(\omega / \tilde{\omega}_0^0) \\
 & \quad \times \sum_{k, \lambda} C^*(k_\lambda, 0) D(k_\lambda, 0) \{ \delta(\omega - \tilde{\omega}_k^\lambda) - \delta(\omega + \tilde{\omega}_k^\lambda) \} \\
 & \quad + 4E^2 \sum_{k, \lambda} [|B^\lambda(k)|^2 + 16g^2 |\beta^\lambda(k)|^2] \sum_k \tilde{N}_k^\lambda \{ \delta(\omega - 2\tilde{\omega}_k^\lambda) \\
 & \quad - \delta(\omega + 2\tilde{\omega}_k^\lambda) \} + (6D_1' - 48gV)^2 E^2 \tilde{N}_0^0 \{ \delta(\omega - 2\Omega)
 \end{aligned}$$

$$\begin{aligned}
& -\delta(\omega + 2\Omega)\} + 24V^2([1 + 3(\tilde{N}_0^0)]^2 \{\delta(\omega - 3\Omega) \\
& -\delta(\omega + 3\Omega)\} - [1 - (\tilde{N}_0^0)^2] \{\delta(\omega - \Omega) - \delta(\omega + \Omega)\}), \quad \dots (8)
\end{aligned}$$

$$\text{where } \delta = \delta_{123} + \delta_{213} + \delta_{321}, \quad \dots (9a)$$

$$\text{with } \delta_{123} = \delta_{k_1, -k_1'} (\delta_{k_2, -k_2'} \delta_{k_3, -k_3'} + \delta_{k_2, -k_3'} \delta_{k_3, -k_2'}), \quad \dots (9b)$$

$$\text{also } \tilde{N}_0^0 = \coth(\eta \Omega_k^\lambda / 2k_B T). \quad \dots (9c)$$

$$\text{and } \tilde{N}_k^\lambda = \coth(\eta \tilde{\omega}_k^\lambda / 2k_B T). \quad \dots (9d)$$

2.2 Curie temperature

The real part of the complex dielectric constant in Eq. (4) now takes the form

$$\epsilon'(\omega) - 1 = -8\pi M_\mu^2(0) \frac{\omega_0^0 [\omega^2 - \nu_0^0(\omega)]}{[\omega^2 - \nu^2(\omega)]^2 + \Gamma_0^0(\omega)}. \quad \dots (10)$$

In the presence of electric field in a doped ferroelectric crystal, the real part of the Green's function given by Eq. (6), gives Cochran's temperature-dependent frequency $\Omega(T)$ as the self-consistent solution of the equation

$$\begin{aligned}
\Omega^2 = & -(\omega_0^0)^2 + 4\omega_0^0 D(0,0) + \omega_0^0 E^2 (96g^2 V - 24gD_1') \\
& + 4\omega_0^0 \bar{Q} + \bar{\Delta}_0^0(\omega) \quad \dots (11)
\end{aligned}$$

$\bar{\Delta}_0^0(\omega)$ is given by Eq. 7(a). Hence by comparing Eqs(11) and (7), one can approximate $\nu(\omega)$ as Ω . For a ferroelectric having cubic symmetry, the Cochran mode frequency Ω is very high compared to the microwave frequency ω , so that $\nu(\omega) \gg \omega$ and no relaxation effects are observed. In paraelectrics, the value of $\epsilon'(\omega)$ is very high compared to those in alkali halides, so that $\epsilon'(\omega) \gg 1$. So neglecting 1 in comparison to $\epsilon'(\omega)$. Eq. (4) thus becomes

$$\epsilon'(\omega) = 8\pi M_\mu^2(0) \omega_0^0 / \nu_0^0(\omega) \quad \dots (12)$$

In a pure crystal we have

$$\epsilon'(\omega) = -8\pi M_\mu^2(0) \omega_0^0 / \nu_0^0(\omega) \quad \dots (13)$$

$$\text{where } \nu_0^0(\omega) = -(\omega_0^0)^2 + 4\omega_0^0 \bar{Q} + \Delta_0^0(\omega) \quad \dots (14)$$

$\Delta_0^0(\omega)$ corresponds to a pure crystal and is given by Eq. 7(a) in the absence of defects and the electric field. For an impure crystal, with the help of Eq. (7)

$$\nu^2(\omega) = \nu_0^0(\omega) + \Delta(\nu_{D,E}^2(\omega)), \quad \dots (15)$$

$$\begin{aligned}
\Delta(\nu_{D,E}^2(\omega)) = & 4\omega_0^0 D(0,0) \\
\text{where } & + 4\omega_0^0 \sum_{k,\lambda} D^2(k_\lambda, 0) \frac{\tilde{\omega}_k^\lambda}{\omega^2 - (\tilde{\omega}_k^\lambda)^2}
\end{aligned}$$

$$\begin{aligned}
& - 4(\omega^2 / \omega_0^0) \sum_{k,\lambda} C^2(k_\lambda, 0) \frac{\tilde{\omega}_k^\lambda}{\omega^2 - (\tilde{\omega}_k^\lambda)^2} \\
& + 4\omega \sum_{k,\lambda} C(k_\lambda, 0) D^*(k_\lambda, 0) \times \frac{\tilde{\omega}_k^\lambda}{\omega^2 - (\tilde{\omega}_k^\lambda)^2} \\
& - 4\omega \sum_{k,\lambda} C^*(k_\lambda, 0) D(k_\lambda, 0) \frac{\tilde{\omega}_k^\lambda}{\omega^2 - (\tilde{\omega}_k^\lambda)^2} + 8E^2 \omega_0^0 \\
& \times \sum_k |\beta^\lambda(k)|^2 \sum_k \tilde{N}_k^\lambda \frac{\tilde{\omega}_k^\lambda}{\omega^2 - (2\tilde{\omega}_k^\lambda)^2} + 128g^2 E^2 \omega_0^0 \sum_k |\beta^\lambda(k)|^2 \sum_k \tilde{N}_k^\lambda \\
& \times \frac{\tilde{\omega}_k^\lambda}{\omega^2 - (\tilde{\omega}_k^\lambda)^2} + \omega_0^0 (6D_1' - 48gV)^2 E^2 \tilde{N}_0^0 \frac{4\Omega}{\omega^2 - (2\Omega)^2} \\
& + 96V^2 \omega_0^0 \left([1 + 3(\tilde{N}_0^0)^2] \frac{3\Omega}{\omega^2 - (3\Omega)^2} - [1 - (\tilde{N}_0^0)^2] \frac{\Omega}{\omega^2 - \Omega^2} \right), \quad \dots (16)
\end{aligned}$$

and

$$\nu_0^0(\omega) = -(\omega_0^0)^2 + \frac{4\omega_0^0}{\pi} \sum_k |\beta^\lambda(k)| \tilde{N}_k^\lambda + \Delta_0^0(\omega) \quad \dots (16a)$$

With the help of Eqs(16) and (16a) the temperature-dependence of $\nu^2(\omega)$ can be written as

$$\begin{aligned}
\nu^2(\omega) = & -(\omega_0^0)^2 + \gamma_1 T + \gamma_2 T^2 + \gamma_3 E^2 T + \omega_0^0 E^2 \\
& \times (96g^2 V - 24gD_1') \pm \Delta(\nu_D^2) + \Delta_{DE}(\omega), \quad \dots (17)
\end{aligned}$$

where $\Delta(\nu_D^2)$ is the temperature independent part of Eq. (16) due to defect and γ_i 's ($i=1,2,3$) denote the temperature and electric field independent terms in

$\nu^2(\omega)$ and depend on the anharmonic force constants and electric dipole moment terms. The T and T^2 dependence of $\nu^2(\omega)$ are due to third and fourth order anharmonicities respectively. $\Delta_{DE}(\omega)$ is the cross term of the defect and electric field.

Thus from Eq. (17), one gets

$$\nu^2(\omega)/\gamma = -\frac{(\omega_0^0)^2}{\gamma} + T + [\Delta(\nu^2_D) + \omega_0^0(96g^2V - 24gD'_1)E^2 + \gamma_2T^2] (1/\gamma), \quad \dots (18)$$

where $\gamma = \gamma_1 + E^2\gamma_3$.

Using Eqs (12) and (18), one gets

$$\epsilon'(\omega) = C/[T - T_c + \xi T^2 + (1/\gamma)\{\Delta(\nu^2_D) + \omega_0^0(96g^2V - 24gD'_1)E^2\}], \quad \dots (19)$$

$$\text{where } C = 8\pi M_\mu^2(0)\omega_0^0/\gamma, \quad \dots (19a)$$

$$T_c = (\omega_0^0)^2/\gamma, \quad \dots (19b)$$

$$\text{and } \xi = \gamma_2/\gamma. \quad \dots (19c)$$

Eq. (19) can be rewritten as,

$$\epsilon'(\omega) = C/[T - T'_c + \xi T^2], \quad \dots (20)$$

$$\text{where } T'_c = T_c + \Delta(T_c), \quad \dots (21)$$

$$\text{with } \Delta(T_c) = -\frac{\Delta(\nu^2_D)}{\gamma} + \{[24gD'_1 - 96g^2V] + (\omega_0^0E^2)/\gamma\} \quad \dots (22)$$

Eq. (22) shows that the change in the Curie temperature depends both on the impurities and the external electric field. $\gamma (= \gamma_1 + E^2\gamma_3)$ depends on the anharmonic coupling constants and electric field. It is evident from Eq. (22) that the change in Curie temperature ΔT_c is a function of mass change due to defect, anharmonic force constants and the applied electric field. In the absence of electric field ($E=0$), ΔT_c depends on the defects and anharmonicities present in the crystal. Clearly this is a combined effect of defects and anharmonicity in the lattice. The term in curly bracket in Eq. (22) gives the influence of external field on ΔT_c and depends on α (first order dipole moment coefficient), D'_1 (third order dipole moment coefficient), γ and V (fourth order soft

phonon anharmonic coefficient). In a pure crystal [$\Delta(\nu^2_D)=0$] the relative magnitudes of these anharmonic coefficients determine the change in Curie temperature in the presence of an electric field. This field dependence is a consequence of the transformation used by Lingwal *et al*¹⁶. It is clear from Eq. (22) that the change in Curie temperature is dependent upon impurity and electric field terms in the presence of anharmonicity.

2.3 Microwave absorption

In the presence of electric field for a defect ferroelectric crystal, using the Green's function given by Eq. (6) for microwave photons [$\omega \ll \nu(\omega)$], the expression for loss tangent is as follows:

$$\tan \delta(\omega) = -\Gamma_0^0(\omega)/\nu_0^0(\omega) \quad \dots (23)$$

$\Gamma_0^0(\omega)/\nu_0^0(\omega)$ corresponds to the half-width associated with the damping of Cochran soft mode. The damping of microwave therefore arises due to the creation of a virtual

Cochran polarization mode excited by the transverse electromagnetic radiation and the subsequently decay into real phonons by scattering from lattice imperfections and third- and fourth-order anharmonicity, in the presence of electric field. From Eq. (18) one can write

$$\nu^2(\omega) = \gamma(T - T'_c + \xi T^2), \quad \dots (24)$$

$$\gamma(T - T'_c + \xi T^2) \tan \delta = -\bar{\Gamma}_0^0(\omega) \quad \dots (25)$$

$$\gamma(T - T'_c + \xi T^2) \tan \delta = a + b'T + d'T^2 \quad \dots (26)$$

where

$$b' = b + cE^2 \quad \dots (27)$$

and b' and d' are the coefficient of T and T^2 terms and a is temperature independent term in Eq. (18). Eq. (26) can also be rewritten as

$$(T - T'_c + \xi T^2) \tan \delta = A + B'T + D'T^2 \quad \dots (28)$$

$$\text{where } A = a/\gamma, B' = b'/\gamma \text{ and } D' = d'/\gamma \quad \dots (29)$$

Eq. (28) gives the microwave tangent loss in a defect ferroelectric crystal subjected to external electric field. The parameter A depends on the impurity constant in the anharmonic crystal and is

zero for a pure crystal. The Eq. (28) is similar to that obtained by Kumar *et al.*²⁴ and Lingwal *et al.*¹⁶

Therefore empirical formula for loss tangent can be written as

$$(T - T_c) \tan \delta = \omega(\alpha + \beta T + \gamma T^2) \quad \dots (30)$$

Here it is seen that $\alpha=0$ for pure single crystal, β and γ are third- and fourth- order anharmonic interaction terms respectively and are temperature dependent which vary linearly with frequency.

2.4 Variation of dielectric loss with frequency

Using Eq. (30) the Dielectric losses for Ba_xSr_{1-x}TiO₃ mixed crystal with different values of x (x=0, 0.5, 0.8) in frequency range 10-70 GHz in the paraelectric phase (at different temperatures) are calculated in this paper. The parameters α , β , γ and T_c for Ba_xSr_{1-x}TiO₃ with corresponding values of x have been taken from Kumar *et al.*²⁴. A summary of these parameter for Ba_xSr_{1-x}TiO₃ is given in Table 1. —

Figs 1(a) to 1(c) show the variation of $\tan \delta$ for Ba_xSr_{1-x}TiO₃ (x=0, 0.5, 0.8) with frequency for a different field strengths. Taking a particular frequency as a reference, it is observed that dielectric loss ($\tan \delta$) increases with increase of electric field in all the cases.

2.5 Variation of dielectric loss with temperature

With the help of relation $(T - T_c) \tan \delta = \omega(\alpha + \beta T + \gamma T^2)$ the dielectric losses for Ba_xSr_{1-x}TiO₃ mixed crystal with different values of x (x=0, 0.5, 0.8) are calculated and loss tangent vs temperature curves for SrTiO₃, Ba_{0.5}Sr_{0.5}TiO₃, Ba_{0.8}Sr_{0.2}TiO₃ are plotted in Figs 2(a) to 2(c) respectively in paraelectric phase at 10 GHz for different biasing fields.

It is evident from Figs 2(a) to 2(c) that the values of $\tan \delta$ increases with the increasing applied biasing field in all the cases of Ba_xSr_{1-x}TiO₃. It is also evident from the figures that when the temperature approaches to the Curie temperature ($T \rightarrow T_c$) i.e. for lower values of $(T - T_c)$ the loss increases more rapidly. The variations are in good agreement with previous experimental and theoretical results of other workers^{15,16,18,25}.

3 Results and Discussion

The calculated values show the comparative variation of loss tangent with frequency and temperature in the presence of external electric field

Table 1—Parameter α , β , γ and T_c for Ba_xSr_{1-x}TiO₃

Crystal	α (GHz ⁻¹ K)	β (GHz ⁻¹ K)	γ (GHz ⁻¹ K)	T_c (K)
SrTiO ₃	0	2.96×10^{-5}	1.16×10^{-7}	37° K
Ba _{0.5} Sr _{0.5} TiO ₃	9.091×10^{-2}	4.09×10^{-5}	1.14×10^{-7}	218° K
Ba _{0.8} Sr _{0.2} TiO ₃	7.273×10^{-2}	4.09×10^{-5}	1.14×10^{-7}	324° K

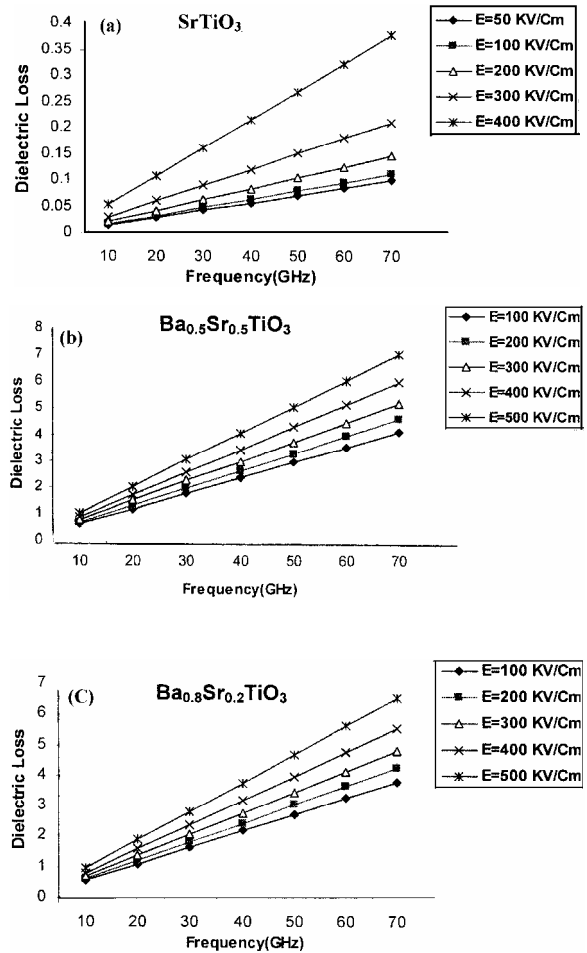


Fig. 1 — Variation of dielectric loss with frequency at different electric field in Ba_xSr_{1-x}TiO₃ ferroelectric perovskites: (a) SrTiO₃, (b) Ba_{0.5}Sr_{0.5}TiO₃, (c) Ba_{0.8}Sr_{0.2}TiO₃.

in Ba_xSr_{1-x}TiO₃. In the present study the Hamiltonian proposed by Silverman²⁶ has been designed in terms of creation and annihilation operator's. To evaluate the higher order correlation functions, the renormalized Hamiltonian has been evaluated using the Green's function technique and Dyson's equation treatment. At microwave frequencies the results are in good agreement with the previous experimental results¹⁵.

Figs 1(a) to 1(c) show the variation of dielectric loss with frequency for different electric field strength of $Ba_xSr_{1-x}TiO_3$ ($x=0, 0.5, 0.8$). It is evident from these figures that at low frequencies the field effect is not remarkable, whereas with increasing frequency the variation of $\tan\delta$ for different values of applied field show good responses. In $Ba_xSr_{1-x}TiO_3$ when $x=0$, loss tangent is increasing with the increase of frequency and the variation is also same for other values of x . As barium increases, the dielectric loss increases continuously. A linear variation of dielectric loss with frequency is in good agreement with previous theoretical and experimental results of many workers^{15,16,18,19,25}

Figs 2(a) to 2(c) show the variation of dielectric loss with temperature in different electric field strengths of $Ba_xSr_{1-x}TiO_3$ for different values of x ($x=0, 0.5, 0.8$). According to our results as

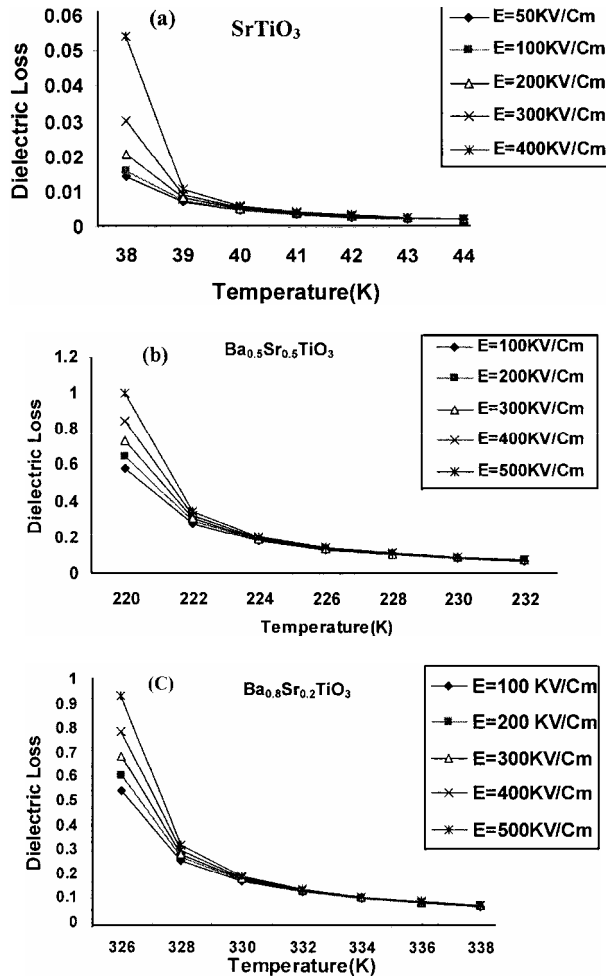


Fig. 2 — Variation of dielectric loss with temperature at different electric field in $Ba_xSr_{1-x}TiO_3$ ferroelectric perovskites: (a) $SrTiO_3$, (b) $Ba_{0.5}Sr_{0.5}TiO_3$, (c) $Ba_{0.8}Sr_{0.2}TiO_3$

temperature approaches towards Curie temperature (i.e. $T \rightarrow T_c$) dielectric loss sharply increases but as difference increases, a sudden fall of dielectric constant is observed¹¹. Our variations are also in good agreement with previous theoretical^{16,18,19,25} and experimental results^{12,15,17,27}. At too high temperatures, the loss tangent deviates strongly from the Curie-Weiss behaviour and increases linearly with temperature. This increase in loss tangent is not due to bulk electronic semi-conduction because this would lead to expect a reciprocal dependence of the frequency on the loss tangent. Third- and fourth-order anharmonicities are held to be responsible for this linear variation of loss tangent. This variation is similar for all concentrations of impurities, i.e. for all values of x and the field's effect ceases at high temperatures.

Experiments give a linear ω dependence for the temperature independent term in the expression for $(T-T_c) \tan \delta$. When mass changes also become appreciable, terms with ω^3 and ω^5 dependence would also occur. The reason why the higher frequency dependences have not been experimentally observed is that these experiments were performed on mixed polycrystalline materials for which contribution Γ_{imp} for scattering from lattice imperfections namely, grain boundaries and lattice defects within the grains, dominates over the contribution Γ_d for scattering from foreign defect atoms. The parameter α is composed of defect Γ_d/r , and imperfections Γ_{imp}/r parts. In this study only Γ_d is calculated. In single mixed crystals of $Ba_xSr_{1-x}TiO_3$, where the contribution Γ_{imp} would vanish, the nonlinear frequency terms in Γ_d could be experimentally detected, provided they lead to losses appreciable compared to anharmonic losses. Experimentally the dielectric properties in $Ba_xSr_{1-x}TiO_3$ are studied in a previous study.²⁸

The electric field induces at low temperature formation of quadrupole and higher moments causing change in the force constants of the bond and hence the Curie temperature, in the paraelectric phase at temperatures well above T_c . Some new phonon scattering processes are found which are not present in the fields absence. These are the electric field induced scattering processes responsible for electric field dependency of the soft ferroelectric mode frequency. Thus in the higher temperature region the electric field effect ceases and the increasing loss arises mainly due to higher order anharmonic terms.

The results obtained are in good agreement with previous theoretical^{16,19,25,26} and experimental results^{12,15,17,27}. Anharmonicity is necessary in these crystals to observe these effects. In the vicinity of the Curie temperature the soft mode frequency [$\Omega \sim (T - T_c)^{1/2}$] becomes vanishingly small and hence the loss tangent increases anomalously.

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