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Microwave losses in ABO_3 type perovskites

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Abstract. Using Green's function method, microwave lossess were theoretically calculated for $BaTiO_3$, $SrTiO_3$ and $KTaO_3$ ferroelectric perovskites. In microwave range, an increase in frequency is followed by an increase in the dielectric loss. In the paraelectric phase, the dielectric loss decreases with increasing temperature showing the Curie-Weiss behaviour of the tangent loss.

Keywords. Ferroelectrics; perovskites; soft-mode; anharmonicity; microwave-loss.

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1. Introduction

The investigation of dielectric properties provides an important approach to the understanding of intra- and -inter molecular interactions, modes of motion and confirmational changes in the macromolecules. The temperature and frequency-dependence of the dielectric loss is the subject of considerable interest due to their extensive use in optical communication, memory display, temperature control devices, ceramic industry, etc. It is well known that several interesting temperature-dependent properties of ferroelectrics result from the temperature-dependence of the low lying transverse optic mode of vibration (Cochran 1969). Microwave losses in displacive ferroelectrics (BT, ST etc.) have been reported experimentally (Rupprecht and Bell 1961, 1962; Rupprecht *et al* 1961). Above the phase transition temperature, the results of the loss measurements can be represented by the temperature and frequency-dependence of the microwave loss tangent ($\tan\delta$) as

$$(T - T_c)\tan\delta = \omega(\alpha + \beta T + \gamma T^2), \tag{1}$$

where the parameter α depends strongly on the defect concentration. Parameters β and γ are third and fourth order anharmonic interaction terms which are temperature-independent but vary linearly with the frequency. Rupprecht and Bell (1961) found that in cubic $SrTiO_3$, the field independent loss tangent goes through a minimum at about 170 K with a much steeper slope on the low temperature side of the minimum than on the high-temperature side. The temperature-dependence of the loss tangent for the damping process is expressed as

$$\tan\delta = \gamma/(\Omega^2 - \omega^2) \approx \gamma/\Omega^2 \sim 1/(T - T_c).$$

Impurity scattering provides the sharp rise of the loss tangent on the low-temperature side of the curve. The microwave frequency was taken from 21–22 GHz.

We have measured experimentally (Baluni and Naithani 1986a) the dielectric constant and the dielectric loss in $BaTiO_3$ and theoretically (Baluni and Naithani 1986b; Panwar *et al* 1989) calculated these properties in ferroelectric solids but have made no numerical calculations. The damping of the microwaves in a pure crystal for which $\alpha = 0$, is due to the damping of the polarization mode by anharmonicities of the lattice vibrations. Temperature-dependence of the loss tangent is a reflection of the temperature-dependence of the polarization mode frequency which is given as

$$\Omega \sim (T - T_c)^{\frac{1}{2}}. \tag{2}$$

Microwave loss obeys the Curie-Weiss law. This may be taken as a direct evidence for the temperature-dependence of the polarization mode frequency. At transition temperature, the frequency of the soft mode tends to zero and the lattice displacement associated with this mode becomes unstable. This explains the anomalous behaviour of the dielectric loss near the phase transition. The earlier studies (Benedict and Durand 1958; Lurio and Stern 1960) on $BaTiO_3$ crystals observed relatively high microwave loss above the Curie temperature. The losses were found to be varying linearly with the frequency. Silverman-Joseph (1963) described a Hamiltonian for displacive ferroelectrics and studied the loss tangent for $SrTiO_3$ and found that coefficients β and γ and hence $\tan\delta$ vary linearly with the frequency ω. $SrTiO_3$ (Rupprecht and Bell 1961), $CaTiO_3$ (Lurio and Herrington 1958), $KTaO_3$, $KTaO_3$: $NaTaO_3$ (Agrawal and Rao 1970) exhibit the same behaviour. Lurio and Herrington (1958) have explained that the loss tangent (in the low frequency range at RT) is proportional to the frequency in the range 3–36 GHz. Davis and Rubin (1953) have investigated the loss tangent of certain mixtures of $Ba_xSr_{1-x}TiO_3$ at 35 GHz frequency above and below the Curie temperature Tani (1969) had explained the critical slowing down of the damping constant in displacive ferroelectrics from the standpoint of the irreversible thermodynamics. In place of tangent loss description, only temperature-dependent damping constant is described. Vinogradov (1963) observed that $\tan\delta$ for inoic crystals with ideal lattice, is weakly dependent on frequency in the region of 10^5 to 10^8 Hz. West (1987) measured the electrical losses ($\tan\delta$) for $BaTiO_3$ ceramic at frequencies up to 2 GHz. The 1 MHz dissipation factor was found to be 0·025. At RT, $\tan\delta$ is almost constant in the frequency range 0·001–10 MHz and in 10 MHz to 10^3 MHz, $\tan\delta$ increases linearly with frequency.

Udagawa (1981) had studied the dielectric dispersion in tetragonal $BaTiO_3$ at RT using one oscillator dielectric fiunction mainly due to soft TO phonons but tangent loss is not studied. Vogt (1982) has not calculated $\tan\delta$ but he estimated the relative damping for cubic BT from hyper Raman spectrum. Fleury and Lazay (1971) have reported temperature-dependence of the Brillouin-Raman spectrum of $BaTiO_3$ using the approximated complex susceptibility. Balagurov (1970) studied the attenuation of critical vibrations and dielectric losses in displacive ferroelectrics theoretically. Naithani (1980) and Panwar *et al* (1989) have expressed dielectric losses theoretically with no numerical estimation.

In the present work, we have theoretically studied the functional dependence of the microwave loss tangent on parameters such as temperature and frequency, using Green's function method (Zubarav 1960) in pure anharmonic ferroelectric (BT, ST and KT) crystals with the help of Pytte's (1970) modified Hamiltonian considering anharmonic effects up to fourth order and have compared the results with that of others.

2. Hamiltonian and Green's function

The modified Hamiltonian (Baluni and Naithani 1986b) which includes the fourth-order anharmonicity due to interactions of the soft mode coordinates, resonant interaction and the scattering terms can be written as

$$H = \frac{1}{4}\sum_k \omega_k^a (A_k^{a+} A_k^a + B_k^{a+} B_k^a) + \frac{1}{4}\sum_k \omega_k^o (A_k^{o+} A_k^o + B_k^{o+} B_k^o)$$
$$+ \frac{1}{4}\omega_o^o (A_o^{o+} A_o^o + B_o^{o+} B_o^o) + \Gamma_1'/2) A_o^{o3} + (\Gamma_2'/4) A_o^{o4} + \frac{1}{2} V A_o^{o2}$$
$$+ \imath |A| \sum_k |F| A_k^a A_o^o + \sum_k |H| A_k^a A_o^{o2}, \tag{3}$$

where the notations used are same as those used by Baluni and Naithani (1986b).

To study the dielectric constant and loss, we introduce the following Green's function for the soft phonon

$$G_o^o(t - t^1) = \ll A_o^o(t);\quad A_o^o(t') \gg_{\omega + \imath\varepsilon}, \tag{4}$$

or

$$G_o^o(\omega + \imath\varepsilon) = G'(\omega) - G''(\omega). \tag{5}$$

Writing the equation of motion for Green's function in (4) with the help of modified Hamiltonian in (3), Fourier transforming and writing it in Dyson's equation form, one obtains

$$G_o^o(\omega + \imath\varepsilon) = \omega_o^o / \pi[\omega^2 - v^2(\omega) + 2\imath\omega\Gamma(\omega)], \tag{6}$$

where

$$v^2(\omega) = -(\omega_o^o)^2 - 2\omega_o^o V + \Delta^o(\omega), \tag{7}$$

$$\Delta^o(\omega) = 18\Gamma_1'^2 N\left[\frac{2\Omega}{\omega^2 - (2\Omega)^2}\right] + 4\Gamma_2'^2\left[(1 + 3N^2)\frac{3\Omega}{[\omega^2 - (3\Omega)^2]}\right.$$
$$\left. - (1 - N^2)\frac{\Omega}{(\omega^2 - \Omega^2)}\right] + 16\sum |H|^2 \times \left[(N_k^a \pm N_k^o)\right.$$
$$\left. \times \frac{\Omega_k^a \pm \Omega_k^o}{[\omega^2 - (\Omega_k^a \pm \Omega_k^o)^2]}\right] - \left[4|A|^2 \sum_k |F|^2 N \frac{\omega}{(\omega^2 - \Omega^2)}\right], \tag{8a}$$

$$\Delta^o(T) = AT + BT^2,$$

$$\Gamma^o(\omega) = 9\pi\Gamma_1'^2 N\{\delta(\omega - 2\Omega) - \delta(\omega + 2\Omega)\}$$
$$+ 2\pi\Gamma_2'^2[(1 + 3N^2)\{\delta(\omega - 3\Omega) + \delta(\omega + 3\Omega)\}$$
$$- (1 - N^2)\{\delta(\omega - \Omega) - \delta(\omega + \Omega)\}]$$
$$+ 8\pi\sum |H|^2 (N_k^a \pm N_k^o) \times [\delta(\omega - \Omega_k^a - \Omega_k^o) - \delta(\omega + \Omega_k^a + \Omega_k^o)]$$
$$+ \pi[-2|A|^2 \sum |F|^2] N \times [\delta(\omega - \Omega) - \delta(\omega + \Omega)], \tag{9a}$$

and

$$\Gamma^o(T) = AT + BT^2, \tag{9b}$$

Equations (8b) and (9b) show the temperature-dependence of shift and width of the

optic phonon respectively. In general, soft mode frequency (Naithani *et al* 1986) may be written as

$$\Omega^2 = r_1 + r_2 T + r_3 T^2,$$

where $v \simeq \Omega$. r_3 is very small when T is not high then,

$$\Omega^2 = r_2(T - T_c), \tag{10}$$

where $T_c(= -r_1/r_2)$ is the phase transition temperature.

3. Dielectric losses

The complex dielectric constant ε is given by:

$$\varepsilon = \varepsilon' - \imath\varepsilon'', \tag{11}$$

The dielectric loss tangent ($\tan\delta$) for the dissipation of power is defined as

$$\tan\delta = \varepsilon''/\varepsilon' = G''(\omega)/G'(\omega). \tag{12}$$

Thus the retarded one phonon Green's function is enough to determine the dielectric susceptibility and hence the dielectric constant and the tangent loss. Separating the real and the imaginary parts $G'(\omega)$ and $G''(\omega)$ of $G(\omega)$ from (6) and then using (12) we get

$$\tan\delta = 2\omega\Gamma_o/(\Omega^2 - \omega^2). \tag{13}$$

Some results of others are given below:

Udagawa (1981):

$$\tan\delta = 2\omega\Gamma_o/(\omega_o^2 - \omega^2), \tag{14}$$

Vogt (1982):

$$\tan\delta = \gamma\Omega/(\Omega_o^2 - \Omega^2), \tag{15}$$

Fleury and Lazay (1971):

$$\tan\delta \approx 2\Gamma_o/(\omega_o^2 - \omega^2), \tag{16}$$

Balagurov (1970):

$$\tan\delta = 2\omega\Gamma/(\omega_c^2 - \omega^2), \tag{17}$$

Panwar (1989) and Naithani (1980):

$$\tan\delta = \Omega\Gamma_o/(\Omega^2 - \omega^2), \tag{18}$$

Here in deriving (14) to (18), different authors have used different methods, approximations and symbols. Equations (14) to (17) are not mentioned in such forms in those papers but these results are presented in terms of the dielectric (complex, real and imaginary) constants. We have written $\tan\delta$ for these results using $\tan\delta = \varepsilon''/\varepsilon'$. Only in (18), the results are given in such forms as written here but no experimental and numerical estimation is made.

The soft mode frequency Ω is very large as compared to microwave frequency ω(as $\omega/\Omega \approx 10^{-3}$) and no relaxation effects are observed. So (13) may be written as

$$\tan\delta \simeq 2\omega\Gamma_o/\Omega^2, \tag{19}$$

with the help of (9b) and (10), (19) may be written as

$$(T - T_c)\tan\delta = \omega(\beta T + \gamma T^2), \tag{20}$$

where

$$\beta = 2A/r_2$$

and

$$\gamma = 2B/r_2. \tag{21}$$

Here β and γ are the characteristics of the microwave losses which are connected to the dielectric material itself and are therefore unavoidable.

3.1 *Frequency-variated microwave losses*

Using (20), we have calculated the microwave losses for pure anharmonic BT, ST and KT crystals in the frequency range 1–35 GHz in paraelectric phase. Parameters β and γ for BT are obtained by best fit of the data (Bornstein 1981) to (20) and for ST these parameters are taken from our previous paper (Deorani *et al* 1990a). Parameters A and B for KT are first calculated using the data (Volkov 1986) in (9b) and then with the help of our earlier work (Deorani *et al* 1990b) (for values of $r_2 \approx K$ there), we obtained the parameters β and γ. A summary of these parameters alongwith T_c for these crystals is given in table 1.

For $BaTiO_3$ crystal, at $T = 130°C$, microwave loss is given by

$$\tan\delta = 2{\cdot}5 \times 10^{-2}\omega. \tag{22}$$

For $SrTiO_3$ at $T = 160\,K$, $\tan\delta = 6{\cdot}26 \times 10^{-5}\omega$, (23)

For $KTaO_3$ at $T = 40\,K$, $\tan\delta = 1{\cdot}47 \times 10^{-4}\omega$. (24)

Here ω's are in GHz. Frequency vs tangent loss curves are plotted in figures 1 and 2 for BT and KT respectively. Curve for ST is already plotted in our earlier paper (Deorani *et al* 1990a).

3.2 *Temperature-dependent microwave loss*

Using (20), we calculated the dielectric losses for these crystals and plotted $\tan\delta$ vs $1/(T - T_c)$ in figures 3, 4 and 5 in paraelectric phase for BT (10 GHz), ST (22 GHz) and KT (10 GHz) respectively.

Table 1. Parameters β, γ and T_c for BT, ST and KT.

Parameters	BT	ST	KT
β	$5{\cdot}83 \times 10^{-4}\,GHz^{-1}$	$2{\cdot}96 \times 10^{-5}\,GHz^{-1}$	$9{\cdot}62 \times 10^{-5}\,GHz^{-1}$
γ	$-1{\cdot}96 \times 10^{-7}\,GHz^{-1}\,K^{-1}$	$1.16 \times 10^{-7}\,GHz^{-1}\,K^{-1}$	$7{\cdot}69 \times 10^{-8}\,GHz^{-1}\,K^{-1}$
T_c (Phase transition temperature)	122°C	37 K	13 K

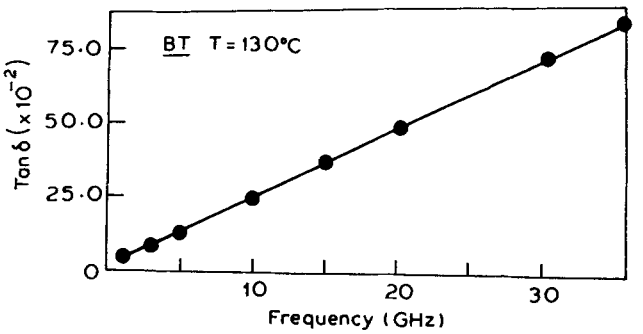

Figure 1. Microwave loss of single crystal $BaTiO_3$ as as a function of frequency at 130°C.

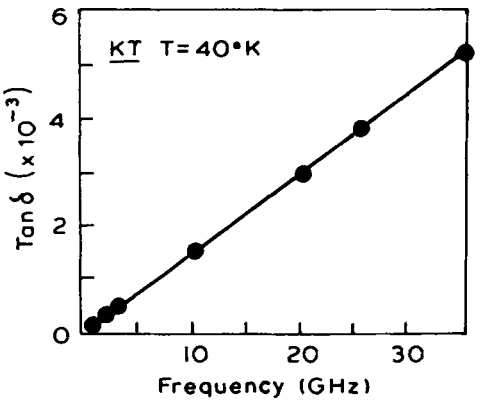

Figure 2. Microwave loss of single crystal $KTaO_3$ as a function of frequency at 40 K.

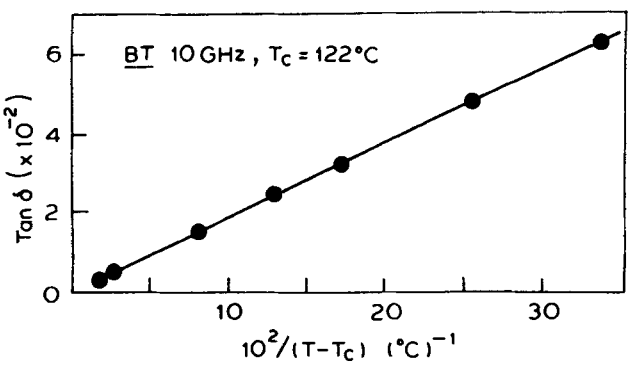

Figure 3. Microwave loss of single crystal $BaTiO_3$ vs $(T - T_c)^{-1}$ at 10 GHz.

4. Discussion and conclusion

The treatment adopted in this work results in the comparative variation of loss tangent at microwave frequencies in $BaTiO_3$, $SrTiO_3$ and $KTaO_3$ with the variation of frequency and temperature. In the present study, the Hamiltonian proposed by Pytte (1970) has been designed in terms of creation and annihilation operators. To evaluate the higher order correlation functions, the renormalized Hamiltonian has been

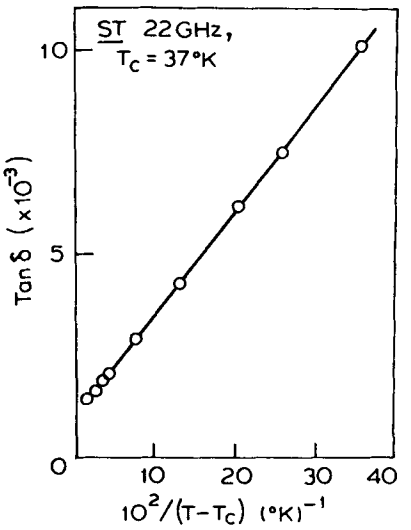

Figure 4. Microwave loss of single crystal $SrTiO_3$ vs$(T - T_c)^{-1}$ at 22 GHz.

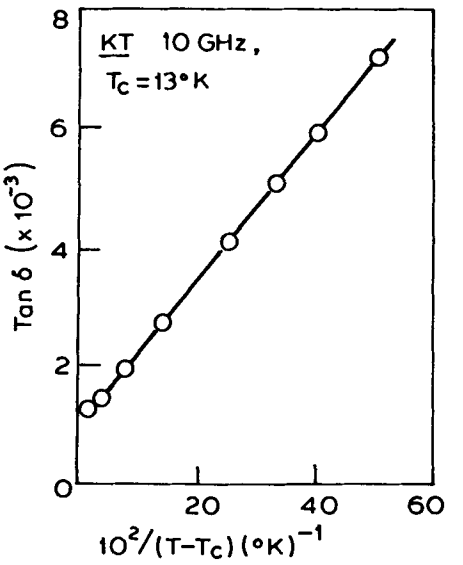

Figure 5. Microwave loss of single crystal $KTaO_3$ vs$(T - T_c)^{-1}$ at 10 GHz.

evaluated using the Green's function technique and Dyson's equation. At microwave frequencies the results are in good agreement with the experimental results.

Thus the technique and approach for obtaining the expression for microwave loss in these perovskites is different from the other workers. We have numerically estimated the loss tangent in BT, ST and KT and have shown a comparative variation of tan δ with frequency and temperature in these crystals.

Equations (22), (23) and (24) alongwith figures 1 and 2 show that microwave losses vary linearly with frequency which is in agreement with the results of Rupprecht and Bell (1962) and others (Banedict and Durand 1958; Vinogradow 1963; West 1987; Lurio and Herrington 1958; Agrawal and Rao 1970; Davis and Rubin 1953). The theoretical results are also in agreement with our experimental results (Baluni and Naithani 1986a). The losses may be explained considering the anharmonic interactions. Due to anharmonic interactions between the phonons, the decay processes take place. For example, third-order anharmonic interaction leads to the decay of a virtual phonon into two real phonons, or the virtual phonon may be destroyed by scattering a thermally excited phonon. Similar processes occur for fourth and higher order interactions. The frequency region of a sharply expressed dispersion of permittivity also corresponds as a rule to the region of marked relaxation dielectric losses.

In figures 3, 4 and 5, the losses show a Curie-Weiss behaviour i.e. they are proportional to $(T - T_c)^{-1}$ in the vicinity of T_c which are in agreement with the results of others (Benedict and Durand 1958; Agrawal and Rao 1970; Davis and Dubin 1953). At too high temperatures, the loss deviates strongly from the Curie-Weiss behaviour and increases linearly with the temperature. This increase in loss is not due to bulk electronic semiconduction because this would lead to expect a reciprocal dependence of frequency on the tangent loss (as losses due to electrical conduction are expressed as $\tan\delta = 1{\cdot}8 \times 10^{10}/f\varepsilon'\rho$, where ρ is the density of the material). Third- and fourth-order anharmonicities are held responsible for this (linear variation of

tan δ) observed tangent loss. In a forthcoming paper, we shall report on the electric field dependent dielectric properties of ABO_3 type crystals.

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