Nonlinearity and Microwave Losses in Cubic Strontium-Titanate

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The complex dielectric constant of single-crystal strontium-titanate has been measured from 90° to 230°K at microwave frequencies. The real part of the dielectric constant consists of a large field-independent contribution which obeys a Curie-Weiss law over the entire range of measurement plus a smaller anisotropic field-dependent contribution. These results are shown to be in qualitative agreement with the theory of ferroelectricity in perovskite structures as proposed by Slater. The observed loss tangent consists of a contribution which is quadratic in an applied biasing field plus a field-independent contribution. The field-independent loss tangent goes through a minimum at about 170° with a much steeper slope on the low-temperature side of the minimum than on the high-temperature side. The origin of the behavior of the field-independent loss tangent is discussed.

THE nonlinear behavior and microwave losses of single crystals of strontium titanate above the Curie temperature have been examined for a wide range of frequencies and temperatures.

It was found that the real part of the dielectric constant, $\epsilon(T,E)$, which was investigated from 90° to 230°K and over a frequency range from 1 kc/sec to 36 kMc/sec, can adequately be described in the form

$$\epsilon(T,E)=\frac{\epsilon(T,0)}{1+(A_{hkl}/C)\epsilon^3(T,0)E^2}, \tag{1}$$

with

$$\epsilon(T,0)=C/(T-T_c). \tag{2}$$

A_{hkl} is an anisotropic "nonlinearity constant," which is essentially frequency and temperature independent, but has a marked dependence upon the direction of an external field E with respect to the crystallographic axes. The values of this constant for the three main crystallographic directions are

$$\begin{aligned} A_{100}&=1.15\times10^{-18} \quad [°\text{K m}^2/\text{v}^2],\\ A_{110}&=0.96\times10^{-18} \quad [°\text{K m}^2/\text{v}^2],\\ A_{111}&=0.69\times10^{-18} \quad [°\text{K m}^2/\text{v}^2]. \end{aligned} \tag{3}$$

Slater's theory[1] of ferroelectricity in perovskite structures predicts a nonlinear behavior of the dielectric constant with the same temperature dependence as appears in Eq. (1). The nonlinear behavior arises in the theory by the introduction of anharmonic restoring forces on the titanium ion when it is displaced from its equilibrium position. The microscopic parameters of the theory can be evaluated and completely determine the constant A_{hkl}. This constant has been calculated for the [100] direction

$$A_{100}=4.5\times10^{-18} \quad [°\text{K m}^2/\text{v}^2]. \tag{4}$$

The order-of-magnitude agreement between the measured and calculated value of the nonlinearity constant, together with the agreement between the observed and predicted temperature dependence of the nonlinear behavior provide strong evidence that lattice anharmonic interactions are indeed responsible for the nonlinearity of the dielectric constant of strontium titanate. These anharmonic interactions are also believed partially responsible for the observed microwave loss.

The imaginary part of the dielectric constant represented by the loss tangent is

$$\tan\delta=\tan\delta_0+\tan\delta_F, \tag{5}$$

where $\tan\delta_0$ and $\tan\delta_F$ are the field-independent and field-dependent loss tangents, respectively.

$\tan\delta_F$ can be described by the expression

$$\tan\delta_F=\omega(B_{hkl}/C)\epsilon^5(T,0)E^2, \tag{6}$$

where B_{hkl} is an anisotropic constant that is temperature, frequency, and field independent. ω is the microwave frequency and E is the dc electric field applied parallel to the probing microwave field.

For example,

$$B_{100}=4.8\times10^{-37} \quad \text{m}^2\,\text{sec}\,°\text{K/v}^2. \tag{7}$$

This is experimentally valid for a frequency range of 2.3 to 6.5 kMc/sec and a temperature range of 90° to 230°K.

$\tan\delta_0$ goes through a minimum (Fig. 1) at about 170°K with a much steeper rise on the low-temperature side of the minimum than on the high-temperature side. A theory[2] for the temperature dependence of the loss tangent has been proposed which agrees with the data to within the experimental accuracy. A sinusoidally varying electric field drives the soft $k=0$ optical mode or polarization mode in a forced vibration. The softness of this mode and the temperature dependence of its frequency are intimately related to the large value of the dielectric constant and its Curie-Weiss behavior, respectively. This point has been discussed in detail by Cochran.[3] The damping of microwaves in the material is believed due to the damping of the polarization mode by impurities or by the anharmonicity of the lattice vibrations. Phonons of microwave pump frequency virtually excited in this mode can be scattered by im-

[1] J. C. Slater, Phys. Rev. **78**, 748 (1950).

[2] B. D. Silverman, Bull. Am. Phys. Soc. **6**, 12 (1961).

[3] W. Cochran, in *Advances in Physics*, edited by N. F. Mott (Taylor and Frances, Ltd., London, 1960), Vol. 9, p. 387.

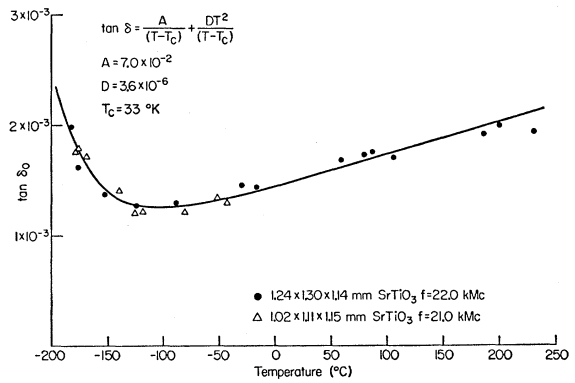

FIG. 1. Temperature dependence of the loss tangent at zero biasing field.

purities into an acoustic mode whose frequency is equal to the microwave pump frequency ω. Such a scattering process is independent of temperature. The temperature dependence of the loss tangent for this damping process is

$$\tan\delta_0=\gamma/(\Omega_T^2-\omega^2)\approx\gamma/\Omega_T^2\sim 1/(T-T_c). \quad (8)$$

T is the absolute temperature; T_c is the Curie temperature; γ is a temperature-independent damping constant; Ω_T is the frequency of the soft transverse polarization mode. The temperature dependence of the loss tangent is a reflection of the temperature dependence of the polarization mode frequency which is written as

$$\Omega_T\sim(T-T_c)^{\frac{1}{2}}. \quad (9)$$

As the temperature is lowered this frequency approaches the microwave pump frequency ω, enhancing the number of microwave phonons excited virtually in the polarization mode. In Eq. (8), ω^2 has been neglected when compared with Ω_T^2. This is justified since

$$\omega/\Omega_T\approx 6\times 10^{-3} \quad \text{at} \quad 90°\text{K}.$$

It has been known for many years that high-loss samples exhibit microwave loss tangents that obey a Curie-Weiss law. We believe this to be direct evidence for the temperature dependence of the polarization mode frequency.

Data obtained for low-loss single-crystal strontium titanate deviate from a Curie-Weiss behavior at higher temperatures. The loss tangent passes through a minimum and increases at sufficiently high temperatures. Losses due to electronic semiconduction have been ruled out as an explanation for this behavior since these high-temperature losses increase with frequency and the measured electrical conductivity is too small. The damping of the polarization mode due to an nth order anharmonic interaction has been found to yield the following loss tangent:

$$\tan\delta=\gamma_n/(\Omega_T^2-\omega^2)\approx\gamma_n/\Omega_T^2\approx T^{n-2}/(T-T_c),$$

where γ_n is the damping constant associated with an nth order anharmonic interaction.

$\tan\delta_0$ is fitted to within the experimental accuracy by using the expression shown in Fig. 1. Impurity scattering provides the sharp rise of the loss tangent on the low-temperature side of the curve. The fourth-order scatterings are believed to provide the more gradual rise on the high-temperature side.

The loss tangent for low-loss polycrystalline Ba-Sr mixtures has also been fitted by the expressions predicted from the theory. To obtain a good fit it has been found that the constant characterizing the impurity contribution to the loss is changed considerably from the single-crystal value, whereas the constant characterizing the anharmonic contribution is unchanged.

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