PHYSICAL REVIEW B VOLUME 59, NUMBER 10 1 MARCH 1999-II

Dielectric and ultrasonic anomalies at 16, 37, and 65 K in $SrTiO_3$

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(Received 4 June 1998)

In this paper we report coincident anomalies in both dielectric response and sound velocities in strontium titanate around three temperatures 16, 37, and 65 K. The anomalies occur in both single-crystal specimens and ceramics, so they cannot be related to grain boundary mechanisms, but they are enhanced by bismuth doping. The results indicate that the dielectric and ultrasonic anomalies are dynamic and not static. The physical nature of the anomalies was briefly discussed. [S0163-1829(99)06109-3]

I. INTRODUCTION

The first report of structural phase transitions in $SrTiO_3$ was a careful x-ray study by Lytle in 1964.[1] He found a phase transition near 110 K, subsequently verified and studied in great detail, but also two others at 35 and 65 K, which have remained enigmatic even until today. Independent confirmation of the lower-temperature ''transitions'' was subsequently provided by Rupprecht and Winter[2] in 1967 and by Sorge and Hegenbarth a few years later[3] via ultrasonic techniques, and by thermal conductivity studies which showed a very large peak at 37 K (Ref. 4) and dielectric permittivity and hysteresis measurements,[5] most recently by Kleemann and Schremmer[6] with dc bias. Also relevant is the study by Bednorz and Müller[7] which showed that 35 K was an upper limit achievable for ferroelectricity in $SrTiO_3$ produced by calcium doping; that is, T_c increases from zero degrees K to 35 K with increasing Ca concentration, but saturated at that temperature at 1.8% Ca, an effect never understood. The 37 K anomaly is perhaps coincidentally the temperature at which a smooth extrapolation of the reciprocal dielectric constant goes to zero from above (a classical ''Curie temperature'').[8] The EPR anomalies around 65 K also were reported.[9,10]

There have occasionally been suggestions that one or more of these anomalies is an example of Cowley's ''type-zero'' phase transitions,[11] marked by an abrupt volume expansion but no symmetry change. However, based on an observation of the sharp dip of the EPR signal in $SrTiO_3$, Müller *et al.*[12] suggested that a spontaneous phase transition into a novel coherent quantum state, would occur at $T<37$ K. In addition, Courtens *et al.* have reported some anomalies around 37 K in the acoustic phonon spectra, and attributed them to second sound.[13]

This paper presents a comparison of dielectric and ultrasonic data on pure and doped strontium titanate at cryogenic temperatures. Anomalies are observed at the same three characteristic temperatures in each case: 16, 37, and 65 K. The connection between the dielectric response at these temperatures and the ultrasonic anomalies, heretofore unreported, is emphasized.

II. EXPERIMENTAL PROCEDURE

The ceramic samples of $(Sr_{1-1.5x}Bi_x)TiO_3$ $(0<x\leqslant 0.0067)$ were prepared by solid state reaction. The x-ray diffraction results indicate that all the samples are single cubic phase and energy dispersion analysis indicates that the Bi concentration is in agreement with the nominal composition, within the experimental error, and that the distribution of Bi is uniform. It was also shown that the dielectric permittivity was independent of the electrodes and of the thickness of the samples. Dielectric complex-permittivity was measured with a Solartron 1260 Impedance Gain-Phase Analyzer and HP4291A Impedance Analyzer. The temperature dependence of dielectric properties was measured in a cryogenic system while the specimen was being heated at a rate of 0.25 or 0.5 K per minute and readings were taken every 0.5 or 1 K. The elastic data measured in single crystal $SrTiO_3$ were previously reported in Ref. 14.

III. RESULTS AND DISCUSSION

Figure 1 shows the temperature (T) dependence of the real and imaginary parts of the permittivity (ϵ' and ϵ'') as a func-

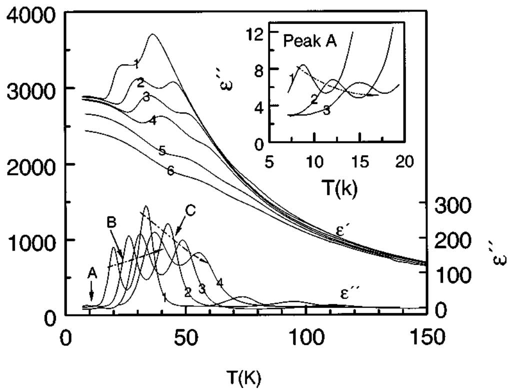

FIG. 1. Temperature dependence of the real and imaginary parts of permittivity (ϵ' and ϵ'') as a function of frequency in $(\mathrm{Sr}_{1-1.5x}\mathrm{Bi}_x)\mathrm{TiO}_3$ with $x=0.002$ at (1) 1 kHz, (2) 100 kHz, (3) 1 MHz, (4) 8 MHz, (5) 110 MHz, and (6) 220 MHz.

tion of frequency for the sample with $x=0.002$. It is evident that there are mainly three sets of permittivity peaks, denoted as peak A, B, and C, with frequency dispersion in Bi:SrTiO_3 from 7 to 300 K. From Fig. 1 it can be clearly seen that with increasing frequency, the permittivity peaks decrease and almost disappear. Figure 2 gives an overall view of the temperature dependence of ϵ'' at 1 MHz for samples with $x=0.002$, 0.0053, and 0.0067, from 7 to 120 K. It shows that the temperature of the three sets of ϵ'' peaks, peaks A, B, and C, are almost independent of the Bi concentration.

Figure 3 superimposes the imaginary part of the dielectric response of ceramic SrTiO_3 at 8 MHz for $x=0.002$ Bi doping, together with the C_L longitudinal sound velocity data (at 8 MHz) for single-crystal strontium titanate.[14,15] Both sets of data show three clear anomalies at around 16 K (peak A), 37 K (peak B), and 56–65 K (peak C).

The coincident anomalies in both dielectric response and sound velocities occur in both single-crystal and ceramic specimens, so they cannot be related to grain boundary mechanisms, but they are enhanced by bismuth doping. In addition, for many ionic oxides with the perovskite structure, the dielectric relaxational behavior is related to the oxygen vacancies.[16–18] In fact, in Bi:SrTiO_3, several dielectric relaxational permittivity peaks closely related to the oxygen vacancies were observed[19]. However, the dielectric anomaly around 16, 37, and 65 K is not related to oxygen vacancies, from the experimental evidence obtained.[19,20]

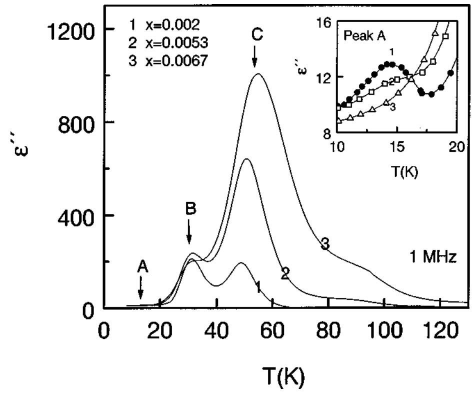

FIG. 2. Temperature dependence of ϵ'' for $(\mathrm{Sr}_{1-1.5x}\mathrm{Bi}_x)\mathrm{TiO}_3$. (1) $x=0.002$, (2) $x=0.0053$, (3) $x=0.0067$ at 1 MHz.

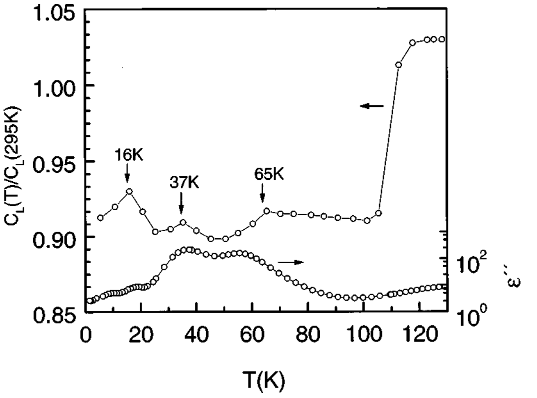

FIG. 3. Temperature dependence of ϵ'' of ceramic SrTiO_3 with $x=0.002$ Bi doping (at 8 MHz), together with the C_L longitudinal sound velocity data (at 8 MHz) for single-crystal SrTiO_3. [The ultrasonic data are from Lei and Ledbetter (Ref. 14).]

From Fig. 1, it can be seen that, for peak A and peak C, the maximum of ϵ'' increases with decreasing frequency; however, for peak B, the maximum of ϵ'' decreases with decreasing frequency, which is common behavior observed in dipolar glasses. Work presented elsewhere[15] shows that the anomalies at 16 and 65 K are dilatational, whereas that at 37 K is a shear. Obviously, for this feature, the dielectric data are in good agreement with the ultrasonic data.

We assume in the present study that all these anomalies are dynamic only and not static (i.e., not a structural phase transition). That means that they are characterized by an order parameter x such that $\langle x^2\rangle$ is nonzero but $\langle x\rangle$ vanishes. Such a dynamic anomaly may be expected to have a response that is characterized by a dispersion of form $A/(1+i\omega\tau)$.

The dielectric response should evidence the same dispersion characteristics. Indeed this is confirmed experimentally, for example, for peak B, the dielectric loss peaks shifting upwards about 17 K in temperature as the measuring frequency is varied from 1 kHz to 8 MHz. In fact, the frequency dependence of the imaginary part of the permittivity shows a near Debye relation (not shown here), indicating the dielectric relaxation being governed by a single relaxation time. The relaxation time was derived from the frequency dependence of the dielectric loss data, which follow the Arrhenius form $\tau=\tau_0\exp[U/k_BT]$. As Bi=0.002–0.0053, for peak C, $\tau_0=(0.8\text{–}1)\times10^{-13}$ sec, $U=\sim62\pm2$ meV (shown in Fig. 4); for peak B, $\tau_0=(0.4\text{–}1)\times10^{-12}$ sec; $U=33\pm1$ meV. The dielectric anomalies also almost disappear at higher frequencies (GHz regime), which agrees with the observation of the Brillouin data at 30 GHz that show no anomalies at these temperatures.[13] All the results above imply that the anomalies are dynamic and not static.

The ultrasonic anomalies recently reported at 16, 37, and 65 K (Ref. 15) have been confirmed by dielectric measurements. These comparisons indicate that the dielectric and ultrasonic anomalies show a clear dynamic character, and the results have some profound implications. First, they show that the earlier publication of elastic anomalies for the single-crystal but multidomain strontium titanate cannot be due to some accidental combination of elastic constants $C_{ij}(T)$ having sharp dips or cusps;[15,21] no dielectric anomalies occur for

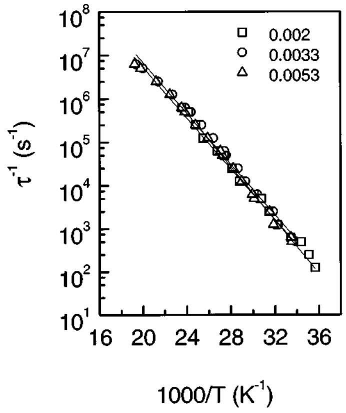

FIG. 4. Temperature dependence of relaxation time (τ) for peak C in $(Sr_{1-1.5x}Bi_x)TiO_3$. (1) $x=0.002$, (2) $x=0.0033$, and (3) $x=0.0053$. The straight lines are fitted to the Arrhenius relation $\tau=\tau_0\exp[U/k_BT]$.

such circumstances. In addition, the second sound model[13,21] should not produce dielectric anomalies at the temperature at which they begin. Secondly, we note that all peaks around 37 K observed here are dynamic, not static. This seems incompatible with the interpretation of the sharp EPR signal dip in $SrTiO_3$, by Müller *et al.* in terms of a coherent quantum state model.[12]

The anomalies exist in both nominally pure $SrTiO_3$ and Bi doped ST. For Bi doped $SrTiO_3$, the temperature (T_m) of the dielectric anomalies does not change with Bi concentration. However, their intensity is roughly proportional to the Bi concentration x. These facts indicate that the anomalies are related to both an intrinsic mechanism and the impurity doping. In Ref. 20, the occurrence of the dielectric peaks in Bi doped ST is attributed to off-center Bi ions. A possible explanation for all of this data is that the dielectric anomalies mainly arise from the defects, off-center Bi ions, which act as dipoles or local polar clusters; the ultrasonic anomalies arise from the elastic domain freezing.[22] Furthermore, the unshifted T_m implies that the off-center Bi ions interact with the intrinsic mechanism—the motion of the ferroelastic domain walls below the antidistortive phase transition at 105 K, which gives a fixed temperature range.

Based on the idea mentioned above, it is reasonable to propose that the sharp loss peak in Fig. 2 is due to local disorder of the off-center Bi ions, and with increasing Bi, the peak broadening as reported in Ref. 20 could be attributed to the overlap of the local disorder regions, as the material becomes a ferroelectric relaxor. Therefore the effects described here may be more easily described by a local disorder model involving Bi ions and probably their nearest-neighbor oxygens.

In addition, we know from work of Balashkova *et al.*[23] and also that of Chrosch and Salje[24] that the domains in $SrTiO_3$ completely freeze out (become immobile) near $T=37$ K. Chrosch and Salje[24] have shown that domain wall density increases more rapidly with decreasing temperature in $SrTiO_3$ than in other known materials. Because the number of density is so large, a significant volume fraction of the crystal will normally consist of the material within the domain walls, even though the domain walls are thin. This material has a lower symmetry than the material within the domain, and it can undergo phase transitions itself.[25] In addition, the domain walls have a net attractive force toward each other.[26] Thus, the walls should produce complicated strain and dielectric effects. The domain-freezing theory of Gridnev[27] predicts that there will be anomalies both at this temperature and also at a higher temperature at which the product of domain wall number (which increases with decreasing T) and domain wall mobility (which decreases with decreasing T) is maximum. In KH_2PO_4 this is 30 K below T_c, in lower-symmetry CsH_2PO_4 it is 60 K below T_c.[28] Thus it is a plausible proposal for the 65 K anomaly, which lies 40 K below $T_0=105$ K in $SrTiO_3$.

This domain wall freezing hypothesis is not incompatible with small volume expansion(s) as original described by Cowley[11] in the general case. This conjecture is also compatible with slight lattice softening due to the sudden availability of certain anharmonic decay channels, as proposed by Scott and Ledbetter,[15] in that any lattice softening as $T=37$ K is approached from below might trigger domain wall motion. However, no detailed model linking these effects has been developed.

The recent experiment on the polarization during field-heating and field-cooling indicates that polarization freezing was observed in the temperature range in which peak B and peak C occur. This supports the conjecture of domain freezing.[29] Second sound is not compatible with our data, nor with the field-dependent Brillouin data recently reported by Watanabe *et al.*[30]

ACKNOWLEDGMENTS

We thank Professor E. Salje for helpful discussions and communications regarding their unpublished data.

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