Dielectric relaxation modes in bismuth-doped SrTiO$_3$:   The relaxor behavior

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(Received 8 September 1998)

The ferroelectric relaxor behavior in Bi-doped SrTiO$_3$ was studied in the temperature range 1.5–300 K and up to 400 MHz. Some interesting results are shown: (1) Typical ferroelectric relaxor behavior develops out of the other impurity relaxation modes. The ferroelectric relaxor peaks occur on the quantum-paraelectric background. The polarization irreversibility effect observed after field cooling or zero-field cooling, and the data of remanent polarization P_r, show that the ferroelectric relaxor behavior is a nonequilibrium phenomenon. (2) The coexistence of the ferroelectric relaxor peak with other impurity modes indicates that there are several kinds of polar clusters which are responsible for different dielectric anomalies in different temperature ranges. This confirms a multicluster state characteristic in ferroelectric relaxors. (3) Near 400 MHz, an additional relaxation process appears, which indicates the possible existence of two polarization processes in a ferroelectric relaxor. [S0163-1829(99)03606-1]

I. INTRODUCTION

In the last two decades, the physical nature of the family of materials called ''ferroelectric relaxors,''[1–3] such as Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (PMN) or Pb(Sc$_{1/2}$Ta$_{1/2}$)O$_3$ (PST), has attracted much attention. Up to date, different explanations have been proposed for the relaxor behavior. For example, a ''dipolar glass'' model was suggested by Viehland *et al.*,[4] while a domain state model was suggested by Westphal, Kleemann, and Glinchuk.[5] Recently, Vugmeister and Rabitz[6] proposed a theory to describe the temperature dependence of the ''relaxor'' behavior. They considered the dielectric relaxor behavior arising from the dynamic response of the polar clusters which exist in the highly polarized host lattice and proposed that the origin of the clusters arises from the collective hopping of off-center ions in multiwell potentials. By taking into account the cluster-cluster interactions and an appropriate distribution of the local fields, they obtained the dielectric response in good agreement with the experimental results.[6] On the other hand, Cheng *et al.*,[7] based on the analysis of the different simulation methods to describe the temperature dependence of the dielectric permittivity at different frequencies, suggested that there are two kinds of polarization processes in ferroelectric relaxors. Clearly the relaxor phenomena are far away from being fully understood.

Pure SrTiO$_3$ (STO) is an intrinsic quantum paraelectric.[8] However, it is reported that ferroelectric order can be induced in STO by the application of external electrical fields or mechanical stresses,[9] or by introducing substitutional defects[10,11] into the lattice. For the latter case, the most common examples are Ca (Refs. 10,11) and Bi doping.[12,13] In Ca-doped STO, Bednorz and Müller[11] observed the occurrence of a permittivity peak and a crossover from the *XY* quantum ferroelectric state, characterized by a sharp permittivity peak, to one with a ''diffusive character'' as the Ca concentration is increased. They suggested that the Ca^{2+} ions occupy off-center positions at the Sr^{2+} sites. The rounded peak of the permittivity was attributed to a random-field induced ferroelectric domain state. For Bi-doped STO, Skanavi *et al.*,[12] Smolenskii *et al.*,[14] Gubkin, Kashtanova, and

Skanavi,[15] and two of the present authors,[13] reported that the rounded permittivity peaks also occur in Bi-doped STO samples.

In the previous paper[16] we showed that the permittivity of Bi-doped STO displays a distinctly different behavior if compared to Ca-doped STO. We observed a variety of dielectric anomalies with frequency dispersion. While the temperatures of the dielectric loss maxima are independent of the Bi concentration x, their amplitudes change strongly with x. Considering the temperature dependence of the dielectric loss, with increasing Bi doping, some of these impurity modes are suppressed and the remaining ones merge into one broad peak which shows the characteristic features found in typical ferroelectric relaxors. It is the aim of the present paper to study the frequency and temperature dependence of this relaxor mode in more detail. In the present paper we show results for $x \geq 0.0033$. The results for smaller x which are dominated by the impurities modes are presented in the previous paper.[16]

II. EXPERIMENTAL DETAILS

We present results on the complex dielectric permittivity at frequencies 20 Hz$\leq \nu \leq$1 GHz and temperatures $1.5 \leq T \leq 300$ K. In addition, in order to characterize the relaxor ferroelectric state, high-field polarization measurements have been performed. For this purpose a modified Sawyer-Tower circuit was used in which the sample was connected in series with a reference capacitor whose capacitance was larger at least by a factor of 1000 than that of the sample. The voltage across the reference capacitor is a measure of the polarization P in the sample, while the voltage across the sample determines the macroscopic field E. For the preparation of the ceramic samples of $(Sr_{1-1.5x}Bi_x)TiO_3$ ($x = 0-0.167$) and the measurement of the complex dielectric constant at low fields, see the previous paper.[16]

III. RESULTS

Figure 1 shows the temperature dependence of the dielectric loss ε'' for $0.0033 \leq x \leq 0.167$, at 100 Hz. In order to

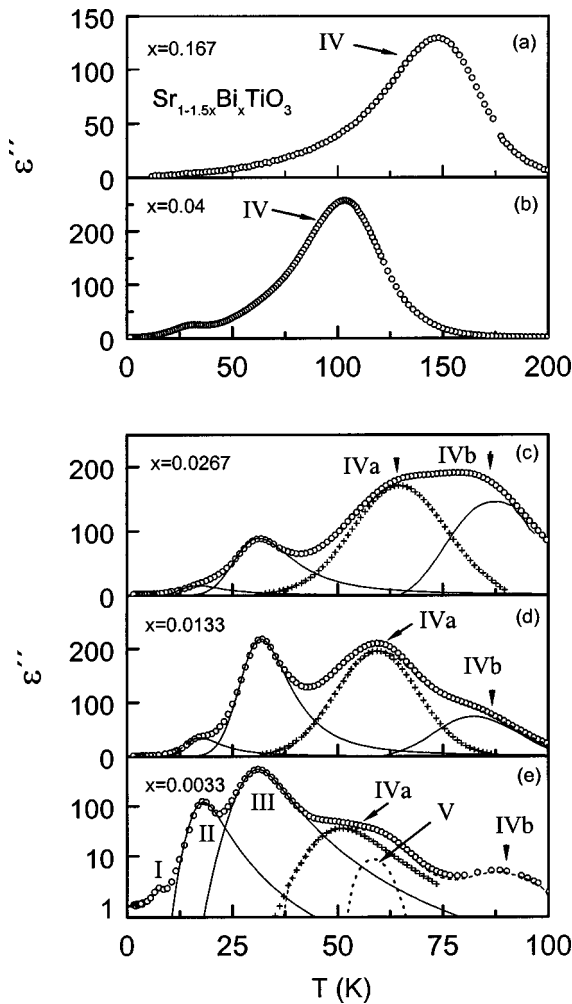FIG. 1. Temperature dependence of the dielectric loss in $(Sr_{1-1.5x}Bi_x)TiO_3$ at 100 Hz for $x=0.0033-0.167$. The roman numbers denote the different relaxation modes (see text). The solid lines: fitting curves for modes II, III, and IVb using the Cole-Cole relation as reported in the previous paper; dashed lines: experimental data subtracted by the fitting curves for modes II and III; dotted line: remainder of peak V as obtained by subtracting data of mode IVa; crosses: relaxor precursor-mode IVa.

FIG. 2. Temperature dependence of ε' and ε'' in $(Sr_{1-1.5x}Bi_x)TiO_3$ ($x=0.04$) at 0.1, 1, 10, 100 kHz, 1, 11, 104, 220, and 400 MHz, (ε': from top; ε'': from left).

keep the figure less complex we have chosen five concentrations for the plots, exhibiting all the typical features. The behavior for the intermediate concentrations fits well in between these results. For $x \geqslant 0.04$, a broad peak has emerged out of a number of impurity modes which were discussed in the previous paper.[16] In the following this peak will be identified as ''relaxor'' peak, typical for the relaxor ferroelectric group of materials. In Fig. 1 it is nicely seen how the relaxor peak develops out of the impurity modes. For $x=0.0033$ [Fig. 1(e)], these modes, which are also seen for the lower concentrations,[16] show up as a variety of relaxation peaks. They have been denoted as I, II, III, and V and were addressed in detail in the previous paper.[16] Peaks II and III are well described by the solid lines which were calculated assuming a Cole-Cole distribution of relaxation times and a thermally activated relaxation time τ. Subtracting the solid lines from the experimental data, leads to the curve shown as dashed line in Fig. 1(e). Obviously, the remaining broad loss peak located in the region 40–70 K is composed of two
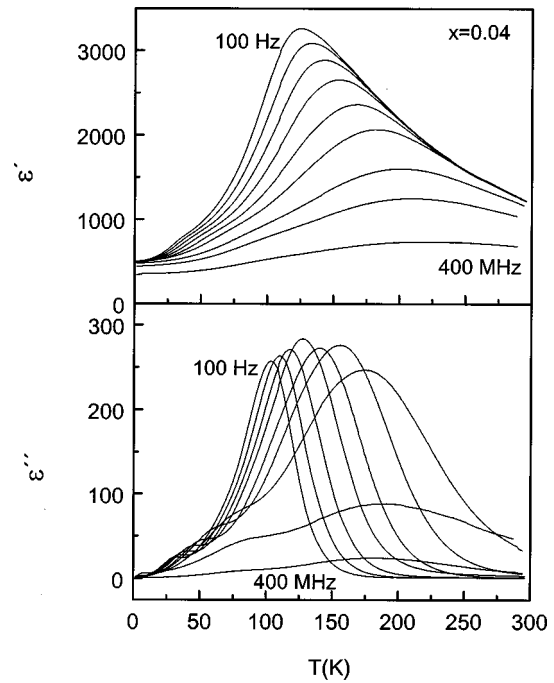
peaks which are indicated as dotted line and pluses in Fig. 1(e). One of these peaks can be identified with peak V already seen at lower x (Ref. 16) and located at about 65 K. [This peak also can be seen in nominally pure $SrTiO_3$ (Refs. 17 and 18).] The second peak, denoted as IVa in the following, is a precursor of the relaxor peak (IV) seen at higher x. A similar subtraction procedure, now also taking into account peak IVb, was also applied for higher x [Figs. 1(c) and 1(d)]. At $x \geqslant 0.0133$, peak V is no longer seen and peak IVa evolves clearly. With increasing x, peak IVa shifts to higher temperatures and starts to merge with peak IVb, located at 87 K. Finally, for $x=0.04$ [Fig. 1(b)] peaks IVa and IVb have merged, the resulting peak IV shifting to higher temperatures with x [Fig. 1(a)].

In order to explore the behavior of the samples in the relaxor region in detail, we chose the sample with $x=0.04$, to plot its temperature dependence of the real and imaginary part of the permittivity in the temperature range 1.5–300 K at different frequencies, as shown in Fig. 2. For frequencies from 100 Hz to 400 MHz, besides a small shoulder due to mode III,[16] a rounded peak occurs in the temperature dependence of the real part of the permittivity ε'. At the temperature of the peak maximum, ε' reaches relatively high values of ~ 3000. At the point of inflection of the $\varepsilon'(T)$ curves, located somewhat below the peak temperature, a loss peak [the relaxor peak IV in Fig. 1(b)] shows up. Both ε' and ε'' exhibit dispersion and the peak temperatures of ε' and ε'' increase with increasing frequency. All these findings indicate a typical ferroelectric relaxor behavior. However, it should be pointed out that at high frequencies, for example, at 1 GHz, no dielectric anomaly is observed (not shown here); this is similar to the observations in the typical ferroelectric relaxors $Sr_{5-x}Ba_xNb_{10}O_{30}$ and $NaNO_2$.[19,20]
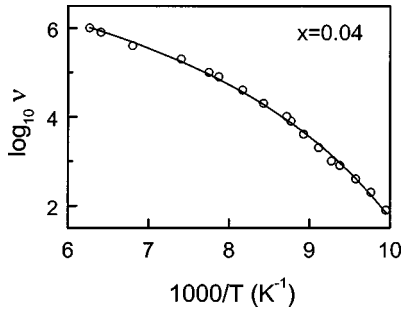
The relaxation rate for the polarization can be estimated

FIG. 3. Temperature dependence of the relaxation rate for $(Sr_{1-1.5x}Bi_x)TiO_3$ with $x=0.04$ [circles: the experimental data; solid line: fitting to the Vogel-Fulcher relation, Eq. (1)].

from the temperature dependence of the imaginary part of the permittivity. The result for $x=0.04$ is plotted in Fig. 3 in Arrehnius representation. The data show clear deviation from thermally activated behavior and can well be fitted to the Vogel-Fulcher relation[21]

$$\nu = \nu_0 \exp\{-E/[k_B(T-T_{VF})]\}, \qquad (1)$$

where ν is the relaxation rate, ν_0 is the pre-exponential term, E is the hindering barrier, T_{VF} is the Vogel-Fulcher temperature and k_B is the Boltzmann constant. The fitting results give $T_{VF}=73$ K, $E=33$ meV, $\nu_0=0.88\times10^8$ Hz. Vogel-Fulcher behavior is often observed in ferroelectric relaxors; see e.g., Ref. 22.

The temperature dependence of the remanent polarization P_r (field cooling at 1 kV/cm, and measured at zero-field heating; cooling and heating rates were 1 K/min) is shown in Fig. 4(a). P_r decreases with increasing temperature and an extrapolation of the slope at the most rapid decrease gives a temperature 92 K. At higher temperature $P_r(T)$ shows a tail-like decrease, smoothly approaching zero. The polarization irreversibility effect which is usually observed in spin glasses and in ferroelectric relaxors, is shown in Fig. 4(b). The data have been obtained after field cooling or zero-field cooling and subsequent field heating at 1 kV/cm; cooling and
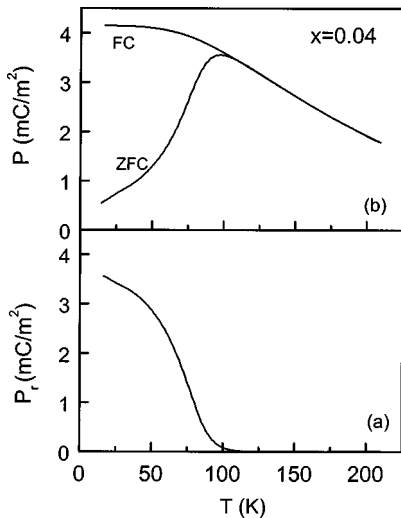

FIG. 4. (a) Temperature dependence of the remanent polarization; (b) temperature dependence of the polarization under field cooling (FC) and zero-field cooling (ZFC) for $(Sr_{1-1.5x}Bi_x)TiO_3$ with $x=0.04$.

heating rates were 1 K/min. Differences between the field cooling (FC) and the zero-field cooling (ZFC) polarization starting at about 100 K are clearly seen. Similar behavior was, e.g., observed in the typical relaxors $Pb(Mg_{1/3}Nb_{2/3})O_3$,[22] La-doped $Pb(Zr,Ti)O_3$,[23] and Li-doped $KTaO_3$.[24] These results show that the relaxor behavior is a nonequilibrium phenomenon. All of these characteristics mentioned above indicate that Bi-doped STO for high Bi concentrations behaves like a typical ferroelectric relaxor.

IV. DISCUSSION

Different from the dielectric anomalies, modes II and III, whose temperature of peak maximum T_m is Bi independent, the "relaxor" peak shifts to higher temperatures with increasing x. As pointed out in the previous paper,[16] the existence of the relaxor peak precursor can be seen already for $x=0.002$. It appears clearly for $x=0.0033$, but its peak amplitude is still small (about 30), however, it increases very quickly to 250 for $x=0.0067$. With further increasing Bi concentration, above $x=0.0267$, this peak becomes dominant, i.e., the system transfers into the so-called relaxor state. From the real part of the permittivity, already in the earlier report,[13] Bi-doped STO was identified as ferroelectric relaxor. The present results on the dielectric loss and the polarization behavior strongly corroborate this conclusion.

As mentioned in the Introduction, a "dipolar glass" model was suggested by Viehland *et al.*[4] which means a disordered characteristic. However, Westphal, Kleemann, and Glinchuk[5] attributed the relaxor behavior in PMN to the presence of domain states induced by quenched random fields. They proposed that the ground state of PMN is ferroelectric, and the random fields induced by the compositional fluctuations lead to the occurrence of the domain state. They suggested that another relaxor system, $K_{1-x}Li_xTaO_3$ for $x \geq 0.026$ undergoes a first-order ferroelectric transition, and it can be described by the domain state induced by random field in terms of the same idea.[25] Höchli and Maglione[26] argued that this is not true for $K_{1-x}Li_xTaO_3$ and suggested that the impurity (Li) modes for $x \leq 0.04$ can be described using spin-glass models; for $x \geq 0.06$ disorder features show up that cannot be attributed to glass models nor to ferroelectricity.[26]

As shown in the previous paper and this paper, for $x = 0.0033-0.0267$, the relaxor peak and the other relaxation modes can be observed on a quantum paraelectric background; this indicates that the relaxor behavior can be superimposed to a paraelectric background. From this point of view, the ground state of the dielectric relaxor seems to be paraelectric. On the other hand, some of the present authors reported[27] that in $Ba(Ti_{1-x}Ce_x)O_3$, being a typical traditional ferroelectric for $x=0$, a relaxor state arises with increasing Ce concentration. For $x=0.2$, the system behaves as a typical ferroelectric relaxor. This result shows that the relaxor state can be also developed from a typical ferroelectric, as also found in the systems $(Ba,Sr)TiO_3$ and $Ba(Ti_{1-x}Sn_x)O_3$.[28,29] These results suggest that for the occurrence of the relaxor behavior, it is not relevant if the beginning state is paraelectric or ferroelectric, but it mainly depends on the appearance of dipoles or dipole clusters and
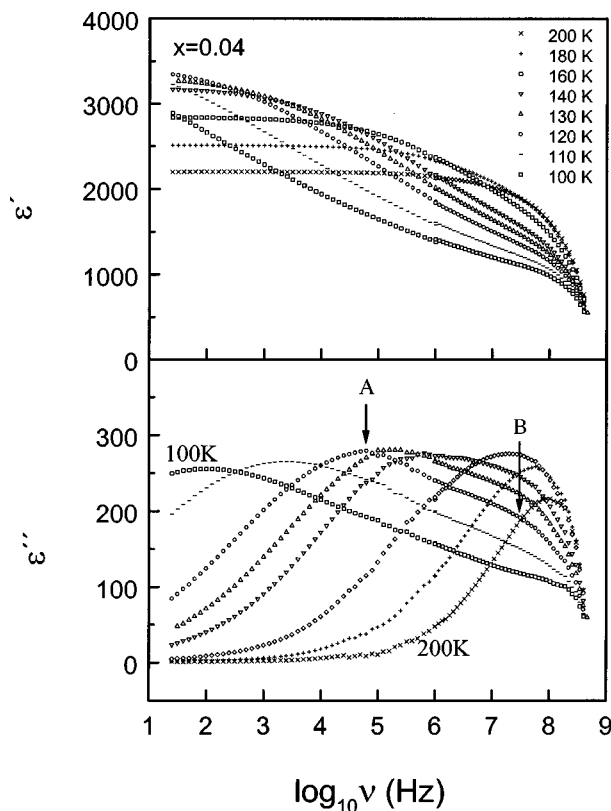
FIG. 5. Frequency dependence of ε' and ε'' for $(Sr_{1-1.5x}Bi_x)TiO_3$ with $x = 0.04$ for various temperatures.

pole clusters become stronger, and some clusteres contribute to the appearance of the relaxor behavior. The increase in the width parameter α [see Fig. 3(c) in the previous paper[16]] confirms this picture. When $x \geqslant 0.04$, the interaction between the polar clusters is strong enough, and the relaxor mode dominates.

As discussed above, these results confirm the multiclusterlike behavior in relaxors. This multicluster behavior perhaps could be described by the modified domain state model[5] or the theory proposed by Vugmeister and Rabitz.[6] Further work is needed to check the validity of the models for Bi-doped STO.

Finally, we also note that the two polarization processes model, suggested by Cheng et al.,[7] only based on a simulation fitting of the $\varepsilon'(T)$ data, perhaps could be supported by the present experimental facts in Bi-doped STO. The possibility of the coexistence of two polarization processes is supported by the frequency dependence of ε' and ε'' in the frequency range 25 Hz–400 MHz shown in Fig. 5. From Fig. 5, it can be seen that there are likely two polarization processes, one is located at lower frequencies, the peak frequency quickly increasing with increasing temperature; another is located at higher frequencies near 100 MHz, almost temperature independent (arrows in Fig. 5). It is interesting that the fast process deduced by Cheng et al.[7] is located at a similar frequency. For very high frequencies the different curves merge together leading to an effectively temperature-independent response. Such a temperature-independent behavior has been also found at ~ 25 GHz in the ferroelectric relaxor $Sr_{5-x}Ba_xNb_{10}O_{30}$ and $NaNO_2$.[19,20] Up to now there is no explanation for this unusual phenomenon. This phenomenon should be further studied; if it is true, it will be helpful to understand the physical nature of the ferroelectric relaxor.

V. CONCLUSIONS

In the present paper, we report several interesting experimental facts for ferroelectric relaxors: (1) The dielectric relaxor anomalies could occur on the quantum paraelectric background in Bi-doped STO. (2) The dielectric relaxor peaks appeared with other dielectric modes around 8, 22, 37, 65, and 87 K (at 100 Hz), whose T_m are independent of the Bi concentration in a wide composition range. The coexistence of the relaxor peaks with other dielectric anomalies indicate that several kinds of polar clusters, which are responsible for different dielectric anomalies in different temperature ranges, coexist in Bi-doped STO. This confirms a multicluster state characteristic in relaxors. (3) The results show the possible existence of two polarization processes in a relaxor, which might be those proposed by Cheng et al.[7]

the interactions between them and/or the impurity with the host lattice.

In addition, the present work shows the coexistence of the relaxor peaks with other dielectric anomalies, some of these modes merging into the relaxor mode. This indicates that several kinds of dipoles or polar clusters, which are responsible for different dielectric modes in different temperature ranges, coexist in Bi-doped STO. It should be stressed that among these various dielectric modes, only the relaxor peak shifts to higher temperatures with increasing Bi concentration, hence the corresponding polar cluster behaves differently from others. As suggested in the previous paper,[16] the dipoles may come from the off-center Bi ions, and the interactions between the dipoles may lead to formation of the dipole clusters which contribute to the dielectric anomalies observed. It seems possible that in Bi-doped STO with increasing Bi doping, at the beginning, Bi impurities give rise to almost noninteracting dipoles or small dipole clusters. This is the case for $x \leqslant 0.002$, where only the modes I, II, III, and V are present, which do not shift with x. With increasing Bi concentration, the interactions between the dipoles or di-

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