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Dielectric polarization processes in Bi:$SrTiO_3$

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1. Introduction

Pure $SrTiO_3$ and $KTaO_3$ are intrinsic quantum paraelectrics [1,2]. Although, from 300 down to 50 K, the temperature dependence of the permittivity of $SrTiO_3$ follows the Curie±Weiss law just as in ordinary ferroelectrics, with a Curie temperature $T_c = 35.5$ K [1]; no permittivity peaks appear with further decreasing temperature, and the permittivity levels-off at a high value at extremely low temperatures. The ferroelectricity is suppressed due to the non-vanishing zero-point motion of fluctuation [1]. However, it is known that permittivity peaks can be induced in $SrTiO_3$ by the application of external electrical field or mechanical stresses [3], or by introducing substitutional impurities [4,6] into the lattice.

For impurity doping studies in quantum paraelectric $SrTiO_3$, the most common examples are Ca doping [4,5] and Bi doping [7±10]. In Ca: $SrTiO_3$, Bednorz and Müller [5] observed the occurrence of a permittivity peak and a crossover from the XY quantum ferroelectric state to a ªdiffusive characterº as the Ca content increased. They suggested that the Ca^{2+} ions occupy off-center positions at the Sr^{2+} sites. The round peak of the permittivity was attributed to a random-field induced ferroelectric domain state. For Bi:ST, in the earlier literature, Skanavi et al. [6], Smolenskii et al. [11], and Gubkin et al. [12], reported that the permittivity peaks were induced by Bi doping, and some of the authors [7] attributed it to the occurrence of the ferroelectricity with diffuse phase transition. Recently, by a systematic study in Bi doped $SrTiO_3$, some of the present authors [8±10] observed five dielectric modes, four T_m-unshifted permittivity peaks, and one ªrelaxorº peak, in the temperature range 1.5±300 K, which is more complicated than the results reported in the earlier literature.

These studies show the complicated dynamic behavior of the doping elements in the quantum paraelectric background and raise many questions to be answered. Further study is needed from both experimental and theoretical interests in order to understand the role of this behavior in dielectric loss mechanism in $SrTiO_3$.

Based on the previous understanding, the authors present further experimental data and try to shed more light on the physical nature of dielectric response in the impurity induced dielectric anomalies in a quantum paraelectric $SrTiO_3$. In the present paper, special attention is paid to the occurrence and analysis of the mechanisms of the dielectric anomalies around 18 and 30 K.

2. Experimental procedure

The ceramic samples of $(Sr_{1-1.5x}Bi_x)TiO_3$ $(x = 0 - 0.04)$

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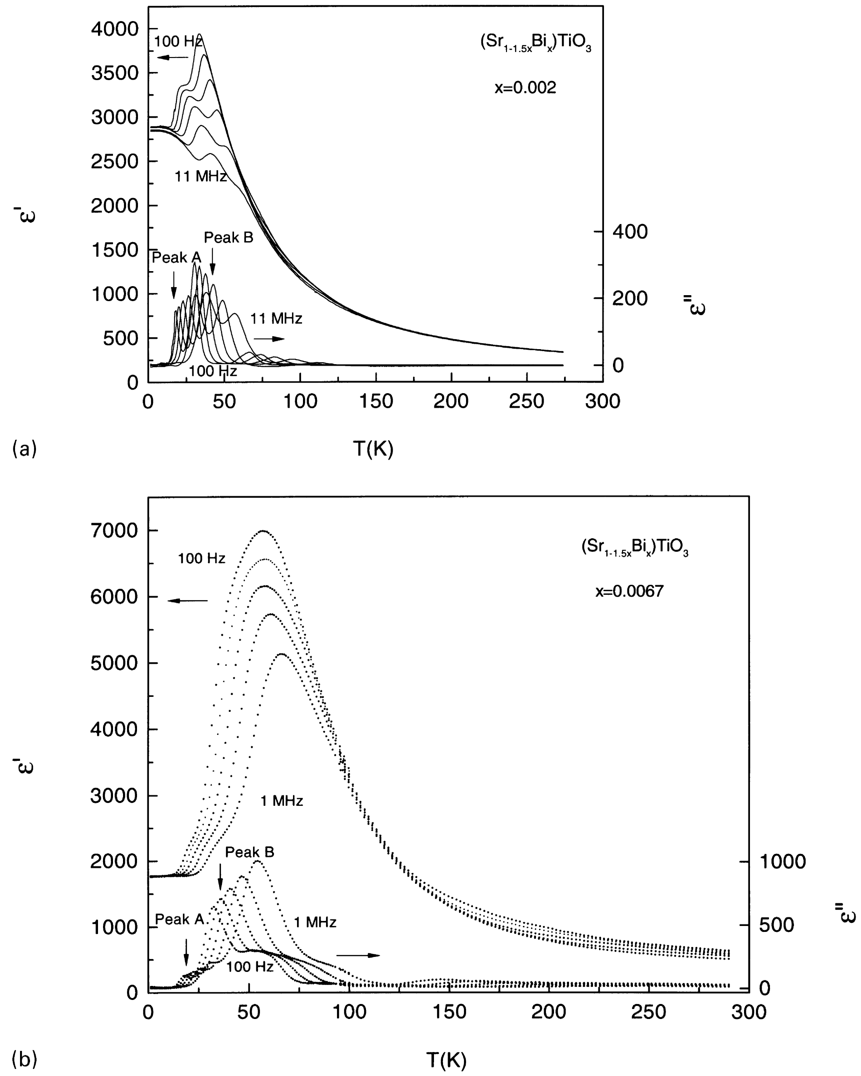

Fig. 1. Temperature dependence of the real and imaginary parts of permittivity (ε' and ε'') as a function of frequency in $(\mathrm{Sr}_{1-1.5x}\mathrm{Bi}_x)\mathrm{TiO}_3$ for: (a) $x = 0.002$; and (b) $x = 0.0067$, at 0.1, 1, 10, 100, 1000, and 11 000 kHz from top to bottom for ε' and from left to right for ε''.

were prepared by the solid state reaction. The samples are of single cubic phase. The detailed process for the samples preparation was described in Refs. [7±10]. Complex dielectric permittivity was measured using HP 4284 and HP 4291A Meters in the frequency range 20 Hz±1 GHz with an ac field of 1 V/mm. The temperature dependence of dielectric properties was measured in a cryostat system in the temperature range 1.5±300 K, while the specimen was being cooled or heated up at a typical cooling/heating rate of 0.4 K/minute and readings were taken at every 1 or 2 K intervals.

3. Results

3.1. Dielectric anomalies

Fig. 1 shows the temperature (T) dependence of the real and imaginary parts of the permittivity (ε' and ε'') as a function of frequency for the $(\mathrm{Sr}_{1-1.5x}\mathrm{Bi}_x)\mathrm{TiO}_3$ ($x = 0.002$ and 0.0067). Fig. 2 shows the temperature dependence of the imaginary part of permittivity, ε'', for the $(\mathrm{Sr}_{1-1.5x}\mathrm{Bi}_x)$-$\mathrm{TiO}_3$ ($x = 0 - 0.04$) at 100 Hz. From Figs. 1 and 2, it is evident that:

1. The distinctive dielectric anomalies occur for both the

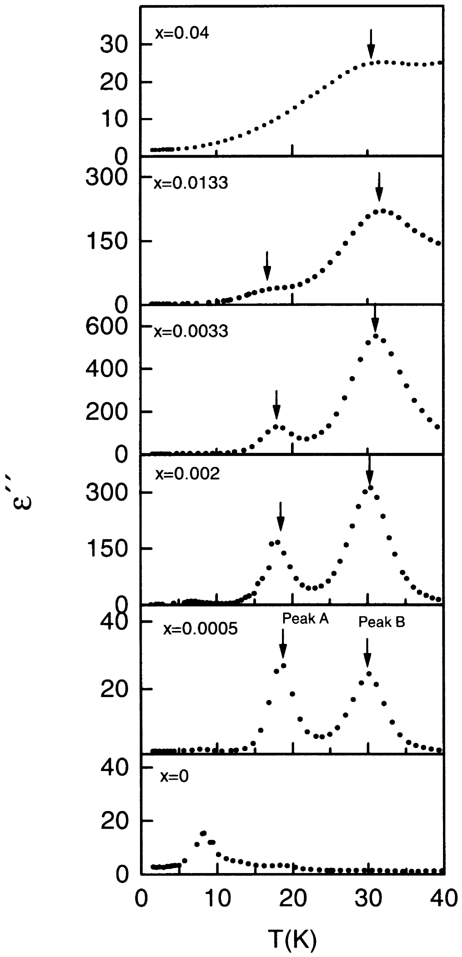

Fig. 2. Temperature dependence of ε'' for $(Sr_{1-1.5x}Bi_x)TiO_3$ with $0 \leq x \leq 0.04$ at 100 Hz.

real and imaginary parts of the permittivity. The dielectric peaks depict frequency dependence, and with temperature of the permittivity maximum (T_m) shifted to higher temperatures with increasing frequency. In ε'' vs T measurement, the peaks occur at ca. 18 and 30 K for 100 Hz, hereafter denoted as peak A and peak B, respectively. As the frequency increases, the dielectric anomalies decrease, and disappear when the measurement frequency exceeds about 10^9 Hz (not shown here).

2. It is observed and should be stressed here that T_m does not change with increasing Bi concentration.
3. The amplitude of the peak A decreases with increasing Bi concentration, and these peaks disappear for $x > 0.0133$, while the amplitude of the peak B, first increases with increasing Bi, reaching a maximum at $x = 0.0067$, and finally disappears when x exceeds 0.133.

Other dielectric anomalies around 8 and 65 K are also observed, which have been previously reported and discussed by several authors [13±15]. Our interpretation of these two anomalies in Bi:$SrTiO_3$ will be given elsewhere. In this paper, we emphasize our discussion of the peaks A and B.

Fig. 3(a) and (b) show the frequency dependence of ε'' of the peaks A and B for $x = 0.002$. Fig. 4 shows the Cole±Cole plot of ε'' vs. ε' of peak B for $x = 0.002$. at 37 K. Figs. 3 and 4 indicate that the dielectric relaxation is almost symmetric in nature. Therefore, the Cole±Cole relation [16]:

$$\varepsilon^* = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty)/[1 + (i\omega\tau)^{1-\alpha}], \qquad (1)$$

was used to describe the dielectric response, where ε_0 is the static permittivity, ε_∞ is the permittivity at high frequency, ω is the angular frequency ($2\pi f$), τ is the mean relaxation time, and α is the angle of the semicircular arc. By fitting this arc with the least square approach, the static permittivity step ($\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty$) and mean relaxation time, as shown in the inset of Fig. 3, were obtained. It is found that the relaxation times for both relaxation processes (peaks A and B) follow the Arrhenius relation, giving the energy barrier $U = 700 \pm 35$ K, and $\tau_0 = \sim 2 \times 10^{-13}$ s for peak A, and $U = 400 \pm 20$ K, and $\tau_0 = \sim 2 \times 10^{-13}$ s for peak A.

Fig. 5 shows the concentration dependence of the width of the peak B (the full width at half maximum of permittivity vs. frequency). It is clear that with increasing Bi concentration, the width of the peak B increases, indicating that the interaction between the Bi ions increases. In other words, it implies that the higher the concentration of the Bi ions, the higher is the interaction among Bi ions.

3.2. *The remnant polarization for* $x = 0.002$

The temperature dependence of the remanant polarization P_r obtained under field cooling (FC) and subsequent zero-field heating (ZFH) is shown in Fig. 6(a) in the temperature range 5±100 K. It can be seen that P_r decreases with increasing temperature and shows two clear steps below 30 K. At higher temperatures $P_r(T)$ slowly approaches zero. The polarization data (P) have been obtained after zero field cooling (ZFC) or field cooling (FC) and subsequent field heating at 1 kV/cm, with cooling and heating rates of 1 K/min. The polarization irreversibility effect that is usually observed in spin glasses and in ferroelectric relaxors starting at ~50 K is observed (Fig. 6(b)). It should be stressed that the two peaks, corresponding to the two steps in P_r, appear during field heating process. The two peaks in Fig. 6(b) and two steps in Fig. 6(a) correspond well to the peaks A and B, respectively. These phenomena are in some way similar to those observed in typical relaxors, such as Li doped $KTaO_3$ [17], $Pb(Mg_{1/3}Nb_{2/3})O_3$ [18], or La doped Pb(Zr,Ti)O_3 [19]. These results probably imply a freezing phenomenon of the polar clusters.

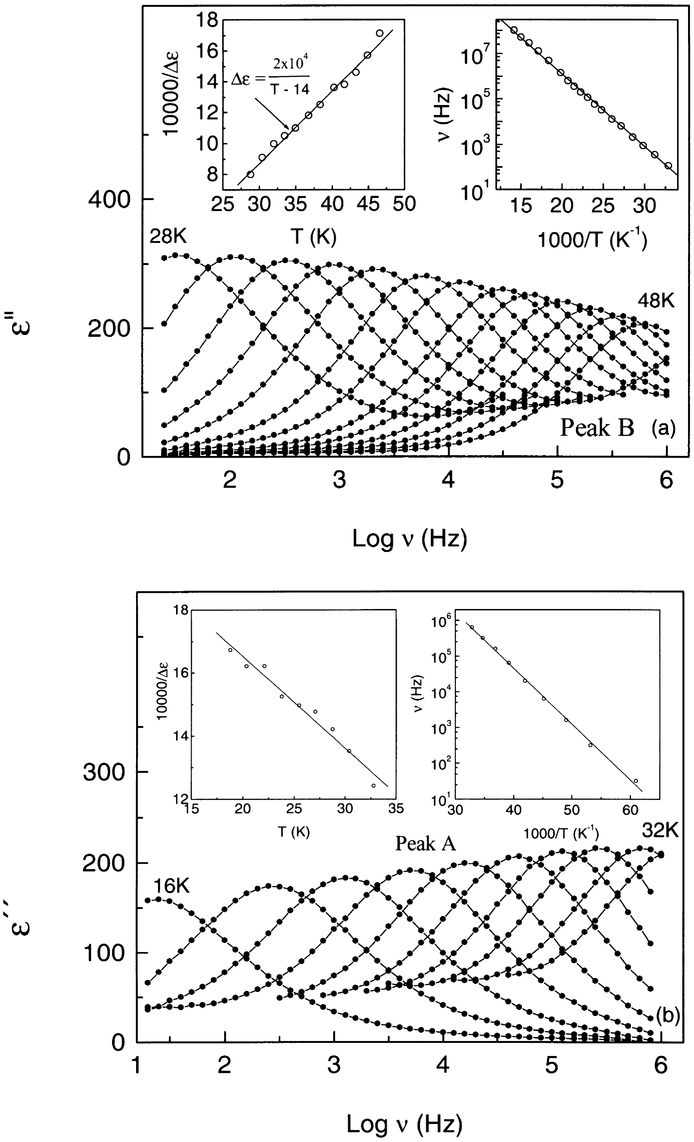

Fig. 3. Frequency dependence of: (a) ε'' for peak B; and (b) peak A for $(\mathrm{Sr}_{1-1.5x}\mathrm{Bi}_x)\mathrm{TiO}_3$ with $x = 0.002$. Insets show the temperature dependence of the relaxation times and of $\Delta\varepsilon^{-1}$ (dotsÐthe experimental data; solid linesÐthe fitting lines).

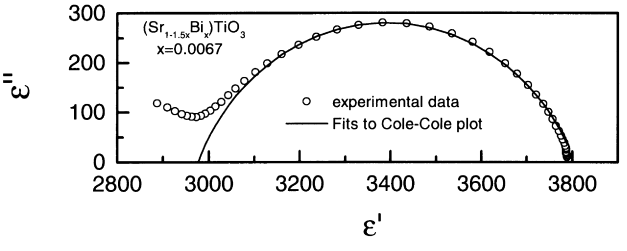

Fig. 4. Cole±Cole plot of ε''vs ε' for peak B of $(\mathrm{Sr}_{1-1.5x}\mathrm{Bi}_x)\mathrm{TiO}_3$ with $x = 0.002$ at 37 K.

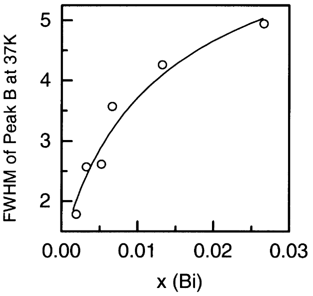

Fig. 5. The Bi concentration dependence of the FWHM (the full width at half maximum of permittivity vs. frequency) for the peak B of $(Sr_{1-1.5x}Bi_x)TiO_3$ at 37 K. The solid line is a guide to the eyes.

4. Discussion

It can be seen from Fig. 1, the extra peaks A and B were induced by Bi doping in addition to the pure $SrTiO_3$-like quantum-paraelectric background. For lower Bi doping concentration, for example, $x = 0.002$ and 0.0033, the impurity is very dilute so that the system could be recognized as an ensemble of non-interacting impurities distributed in a highly polarizable host lattice. If so, in a simple Langevin model, the independent hopping of Bi ions between symmetry-related wells would lead to a relaxation step

$$\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty = np^2/(3k_B T\varepsilon_0) = nq^2\delta^2/(3k_B T\varepsilon_0) \qquad (2)$$

where n is the density of the polarization species, δ is the hopping distance, q is the charge of the Bi, k_B is the Boltzmann's constant and ε_0 is the free space permittivity. Accordingly, for $x = 0.0033$, $n = 5.54 \times 10^{25}\ m^{-3}$ and $\Delta\varepsilon = 2454$ ($T = 36$ K), and for Bi^{3+}, $q = 3$. Substituting all the parameters into Eq. (1), we get $\delta = 1.58$ nm. Obviously, the value of hopping distance, $\delta = 1.58$ nm, is too high to realize for Bi hopping.

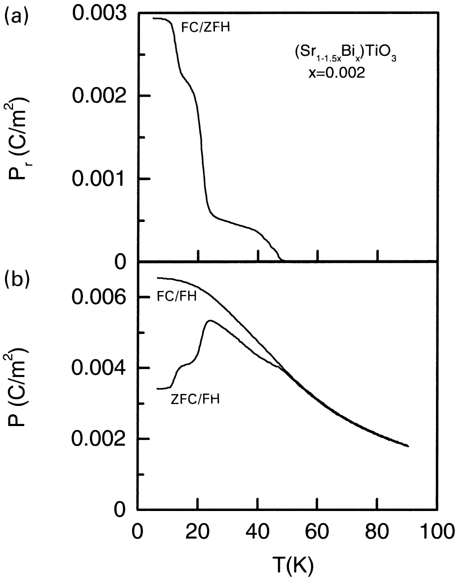

Fig. 6. Temperature dependence of: (a) the remnant polarization under field-cooling/zero-field heating (FC/ZFH); and (b) the polarization under field-cooling/field heating (FC/FH) and zero field-cooling/field heating (ZFC/FH) at 1 kV/cm for $(Sr_{1-1.5x}Bi_x)TiO_3$ with $x = 0.002$. The data obtained form the measurement of hysteresis loop at 1 Hz.

Alternatively, if we consider that the Bi ions polarize the unit cells, as in the case of Nb doped $KTaO_3$ in which it is reported that the Nb ions polarize several unit cells [20], and the relaxation step is related to the local polar clusters with polarization p_s and the linear diameter L of the clusters: $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty = p_s^2 L^2/3k_B T\varepsilon_0$. For $x = 0.0033$, by using $p_s = 0.31\ \mu C\ cm^{-2}$ (obtained from the measurement of polarization [7]), we can obtain that $L = 10.6$ nm, i.e. roughly 27 unit cells for the peak B; $L = 5.78$ nm, i.e. roughly 15 unit cells for the peak A. The size of the cluster, 10.6 and 5.78 nm is apparently too large. If we estimate for the density of the Bi in ST, for $x = 0.0033$, we have $L = 2.61$ nm. Hence the size of the clusters, $L = 10.6$ or 5.78 nm, implies that the clusters should be percolative in nature.

Based on these estimations, we propose the interaction between the impurity Bi and the vibration mode of the host lattice is necessary to account for the dielectric step of the peaks A and B. The theoretical and experimental work suggested that the enhancement of the polar moment of the impurities should be taken into account in the doped host lattice with high polarizability. For example, Stacchiotti and Migoni [21] suggested that the polar moment of off-center Li should be increased owing to the lattice interaction in Li doped $KTaO_3$. The present work also indicates that the same situation should be considered for Bi doped $SrTiO_3$, i.e. the Bi dipolar moment should be enhanced through the interaction possibly with the soft mode in $SrTiO_3$.

However, a question arises as to what the possible picture is for this interaction? At first glance, the very important experimental fact is that the temperature of the peaks A and B do not change regardless of the large variation of Bi content. This suggests that an "intrinsic" mechanism should be involved.

It is reminiscent of the theoretical model for explaining the "central peak" in $SrTiO_3$, developed by Halperin and Varma [22], in which the impurity mode interaction with the soft antiferrodistortive mode for $T_p = 105$ K structural phase transition was considered. They divided the impurities into relaxing defects and frozen defects; the relaxing defects shift phase transition to higher temperatures, and frozen defects act just the opposite. In the present work, we could consider that the Bi impurities interact with the soft ferroelectric mode at $T_c = {\sim}0$ K. In fact, it is well known, for pure ST, there are a ferroelectric soft mode (E_u) and two antiferrodistortive modes ($E_g + A_{1g}$), below 105 K, and two accidentally crosses between them at ca. 30 and 65 K [15].

Recently, a detailed study on the phonon modes in Ca doped $SrTiO_3$ was carried out by Kleemann et al. [23]. They also showed that the first-order TO_1 soft mode crosses the two antiferrodistortive modes ($E_g + A_{1g}$), and give two characteristic frequency points. In fact, the polydispersive behavior observed by Kleemann et al. in Ca doped $SrTiO_3$, with $Ca = 0.002$ and 0.058 [24] implies that the polydispersive dielectric responses might correspond to the multi-crossing frequency points. It is reasonable to assume that the Bi doping may also cause these crossing frequency points, and give some dynamic responses. Such dynamic anomalies could be expected to have a relaxational response which is true in this work.

These results indicate that for $SrTiO_3$, at low temperature ($T < \sim 70$ K), a very small amount of impurity or defects (in the present work, the minimum impurity is $Bi = 500$ ppm) will cause dielectric anomalies, and high dielectric loss peaks. Combining this result with observation of dielectric loss peaks in nominally pure single crystal $SrTiO_3$, this implies that for high polarizibility $SrTiO_3$ host lattice, very dilute "external impurity" and/or some "intrinsic defects", such as oxygen vacancies, reduced Ti ions (Ti^{3+}), local strain, dislocations and domain walls, will lead to an occurrence of the dielectric anomalies, especially, in imaginary part of permittivity, hence giving a high dielectric loss.

5. Conclusions

We observed the dielectric anomalies at 18 and 30 K that are due to Bi doping; however, T_m of those anomalies are independent of Bi dopant level. The dielectric permittivity peaks are found to be frequency dispersive, and the relaxation rate follows the Arrehnius law. The dynamics of the Bi ions around 18 and 30 K were attributed to the effect of off-center ions that form the micro-polar-clusters in a highly polarizable host lattice of $SrTiO_3$, and the high permittivity step in Bi doped $SrTiO_3$ was attributed to enhancement of interaction of the polar moments of the Bi impurities with the soft mode in $SrTiO_3$.

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