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Phonon-coupled impurity dielectric modes in $Sr_{1-1.5x}Bi_xTiO_3$

Chen Ang* and Zhi Yu*

Department of Physics and Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China

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$SrTiO_3$ (ST) doped with Bi shows three Bi-induced dielectric modes (modes *A*, *B*, and *C*) that are superimposed upon the quantum paraelectric behavior of pure ST. In ST doped with low concentration Bi, the modes *A* and *B* exhibit dielectric behavior arising from noninteracting polar clusters. The evidence of the dielectric modes coupling with optical phonons is observed from Raman spectra. The dielectric steps induced by Bi doping can be well described by the modified Debye-Langevin model involving the correlation effect of Bi ions via interaction with the optical phonons of the host lattice. With higher Bi concentration, modes *A* and *B* merge into a ferroelectric-relaxor mode, mode *C*, showing an evolution process towards ferroelectric relaxor.

Two materials in nature, $SrTiO_3$ (ST) and $KTaO_3$ (KT), display quantum paraelectric behavior (QPB), i.e., pure ST or KT exhibits the continuously increasing dielectric permittivity with decreasing temperature until 4 K, and then shows the leveling off of the permittivity to near 0 K.[1–4] It is well known that deliberately doping leads to permittivity peaks occurring in both ST and KT,[5–8] but the physical interpretations of the induced permittivity peaks are unclear.[7–10] Relevant theoretical models[11,12] were developed based on the conjecture that dipole impurities can at certain concentrations induce ferroelectric instability. The theoretical critical concentration of impurity for the occurrence of the long range order is, however, far lower than the experimental value.[11,12]

On the other hand, the ultrasonic, electron spin resonance and dielectric anomalies around 37 K, 65 K, and 10 K were reported in nominally pure and doped ST.[13–18] Various models, including the coherent quantum state,[16] the second sound,[17] and anharmonic phonon interaction,[18] have been proposed. However, the physical nature is still a subject of controversy. All this indicates that the physics in nominally pure and doped quantum paraelectric ST or KT needs further study.

Recently, the present authors have reported that two dielectric modes induced by Bi doping in ST,[13–15] whose T_m (temperature of the permittivity maximum) is independent of Bi concentration, implying that some ‘‘intrinsic’’ mechanisms are involved. In this paper, we report some additional results in Bi-doped ST: the evidence of the dielectric modes coupling with optical phonons is pointed out; the dielectric behavior can be described by the modified Debye-Langevin model; the upper limit of the displacement of ~0.5–0.7 Å for off-center Bi ions is obtained; an evolution from impurity-dielectric modes towards the ferroelectric-relaxor mode with increasing Bi concentration, and all the dielectric anomalies being superimposed on the background of the QPB are emphasized.

The dielectric properties of $Sr_{1-1.5x}Bi_xTiO_3$ ($x=0-0.04$) were measured with an HP 4284A Meter in the frequency range 20 Hz–1 MHz in the temperature range 1.5–300 K. X-ray diffraction, scanning electronic microscopy (SEM), and x-ray line profile analysis indicated that the samples are single cubic phase and the Bi concentration is in agreement with the nominal composition within the experimental error, and that the distribution of Bi atoms is uniform. The results also confirmed that Bi ions are located at Sr sites.

The temperature dependence of the permittivity of the $Sr_{1-1.5x}Bi_xTiO_3$ ($x=0-0.04$) is plotted in Figs. 1 and 2. The evolution of the dielectric behavior with increasing Bi concentration is clearly observed.

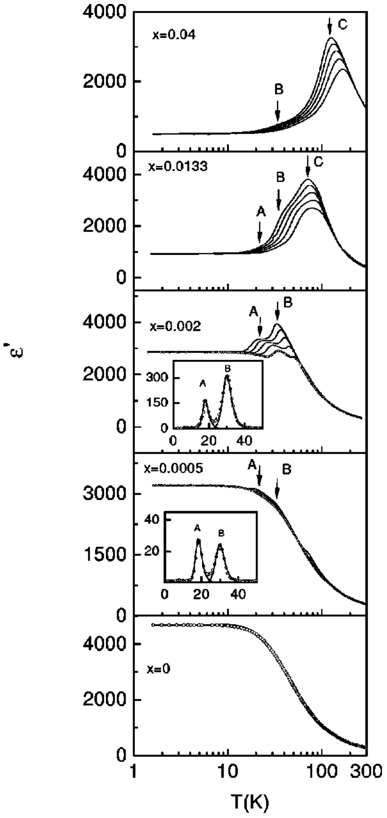

FIG. 1. Temperature dependence of ϵ' for $Sr_{1-1.5x}Bi_xTiO_3$ with $x=0-0.04$ at 0.1, 1, 10, 100, and 1000 kHz, from upper to bottom; open circles: experimental data; solid curves: Fits to the Barrett relation. The inset shows the ϵ'' vs T at 0.1 kHz; open circles: experimental data; solid curves: calculated data according to Eq. (3).

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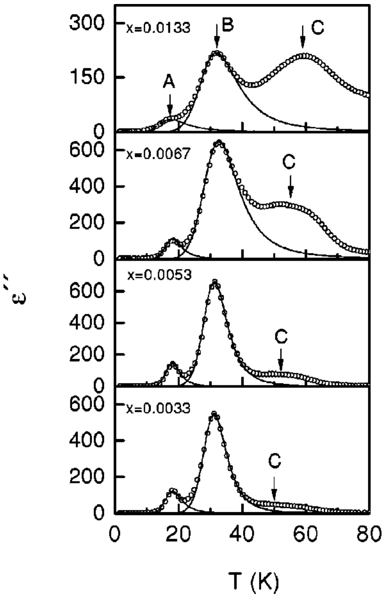

FIG. 2. Temperature dependence of ϵ''; open circles: experimental data; solid curves: calculated data according to Eq. (3).

(1). There are several dielectric modes induced by Bi doping, which are superimposed on the background of the pure ST-like QPB. The distinct leveling off of the permittivity at low temperatures i.e., the QPB, can be fitted to the Barrett relation:[4] $\epsilon' = C/[(T_1/2)\coth(T_1/2T) - T_0]$ with $T_1 = 84$ K, $T_0 = 16.9$ K, and $C = 8\times10^4$ K for $x = 0.0005$; $T_1 = 84$ K, $T_0 = 12.4$ K, and $C = 8\times10^4$ K for $x = 0.001$, etc. (in the present work, for pure ST, $T_1 = 84$ K, $T_0 = 25.1$ K, and $C = 8\times10^4$ K are obtained).

(2). For low concentration Bi doping ($x \leqslant 0.002$), only two dielectric anomalies occur in both ϵ' and ϵ'' (denoted as modes *A* and *B*, respectively). It should be stressed that although modes *A* and *B* are frequency dependent, their T_m (the ϵ'' maximum temperature) at a certain frequency does not change with increasing Bi concentration. However, the amplitudes of modes *A* and *B* increase first with increasing Bi concentration, and reach the maximum at $x = 0.0053$ for mode *A* and at $x = 0.001$ for mode *B*, then decrease. The modes disappear at $x = 0.02$ for mode *A* and at $x = 0.1$ for mode *B*.

(3). With increasing Bi concentration as *x* exceeds 0.002, in addition to modes *A* and *B*, mode *C* occurs, whose T_m increases with increasing Bi concentration. For ϵ', mode *C* overlaps with mode *B*, however, the corresponding ϵ'' for mode *C* is well separated from mode B. The mode *C* increases quickly and dominates above $x = 0.0267$.

It is found that the relaxation times τ for modes *A* and *B* strictly follows the Arrhenius law in the frequency range 10–10^9 Hz; $\tau = \tau_0\exp(E/k_BT)$. The energy barrier *E* and τ_0 were found to be $E_A = 33\pm1$ meV and $\tau_{0,A} = 6\times10^{-12}$ s, and $E_B = 62\pm2$ meV and $\tau_{0,B} = 0.6\times10^{-12}$ s, respectively. However, for mode C with Bi concentration-dependent T_m, τ follows the Vogel-Fulcher law,[19] $\tau = \tau_0\exp[U/k_B(T - T_f)]$. For example, the best fit gives parameters $\tau_0 = 10^{-9}$ s, $T_f = 70$ K for $x = 0.04$, and $\tau_0 = 10^{-9}$ s, $T_f = 50$ K, for $x = 0.0133$. That is, mode *C* displays typical ‘‘relaxor’’ behavior, which has been described in Ref. 15. In this letter, we mainly discuss modes *A* and *B*.

What are the physical mechanisms of modes *A* and *B*? First, experimental fact shows that modes *A* and *B* are induced by Bi doping. Second, the temperature T_m of the modes *A* and *B* does not change regardless of the large variation of Bi content, implying that an ‘‘intrinsic’’ mechanism is involved. The possibility of the ferroelectricity can be excluded due to the Bi concentration independence of T_m.

The symmetric profile of the frequency dependence of ϵ'' implies that a Debye-like impurity dielectric relaxation process may exist.[15] Assuming that the excess polarization comes from the motion of the off-center Bi ions, the dipole polarization moment *p* associated with the dielectric permittivity is given in a simple Debye-Langevin model,[20]

$$\triangle\epsilon = \epsilon_0' - \epsilon_\infty' = np^2/3k_BT\epsilon_0, \tag{1}$$

where ϵ_s' is the static permittivity, ϵ_∞' is the permittivity at the optical frequency, the polarization moment $p = q\delta$ ($q = 3e$ for Bi^{3+} ions, *e* is an electron charge, and δ is displacement of Bi ions), k_B is Boltzmann constant, ϵ_0 is the free space permittivity, *T* is the temperature, and *n* is density of the dipoles. For $x = 0.0053$, $n = 8.86\times10^{25}$ m^{-3}, $\triangle\epsilon = 2980$ ($T = 36$ K) for mode *B*. Substituting these parameters into Eq. (1), we get $\delta_B = 13.8$ Å. Similarly, for the six samples with different Bi concentrations in the range of $x = 0.0005 - 0.0067$, we obtain $\delta_B = 13.8\pm2$ Å for mode *B* and $\delta_A = 6.5\pm1.5$ Å for mode *A*. The almost uniform values of δ_A and δ_B for these samples indicate that the Debye-like impurity dielectric relaxation is reasonable. However, the values seem too large to realize for the motion of Bi ions. Therefore, these dielectric relaxations are expected to be related to the cooperative motion of Bi ions.

Many experimental results reported in the literature indicate that the simple Debye-Langevin model cannot explain the high dielectric polarization steps, and hence an enhancement factor has to be taken into account to obtain a reasonable explanation.[21,22] The theoretical work has been carried out by Vugmeister and Glinchuk,[11] Stacchiotti and Migoni,[12] and the high permittivity induced in Li-doped $\mathrm{KTaO_3}$ was attributed to the enhancement effect of the effective polarization moment caused by the interaction between the impurities and the host lattice via the optical phonons.

In this work, an enhancement factor *N* is introduced into the Debye-Langiven model, i.e., an effective polarization moment $p^* = Np$ is taken into account. The permittivity step is expressed as

$$\triangle\epsilon = n(Nq\delta)^2/3k_BT\epsilon_0, \tag{2}$$

where *N* is an empirical parameter that depends mainly on the host lattice and the impurities. In this work, taking $N = 20$, we obtain $\delta_B = 0.69\pm0.1$ Å for mode *B* and $\delta_A = 0.33\pm0.08$ Å for mode *A*. Using the values δ_B and δ_A, and substituting $\triangle\epsilon = n(Nq\delta)^2/3k_BT\epsilon_0$ into the Cole-Cole equation,[23] we obtain,

$$\epsilon(\delta,T,\omega) = \epsilon_\infty + mn(Nq\delta)^2/3k_BT\epsilon_0[1 + (i\omega\tau)^{1-\alpha}], \tag{3}$$

where τ is the relaxation time for the dielectric modes, ω is the angry frequency, α is the width parameter leading to symmetric broadening of the Debye relaxation, and *m* is a constant. The calculated curves of the temperature depen-

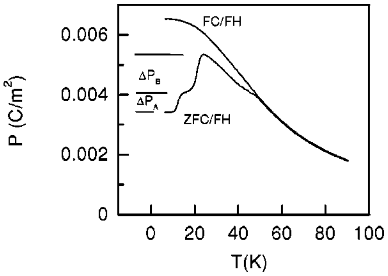

FIG. 3. Temperature dependence of the polarization under zero-field cooling/field heating (ZFC/FH) and field cooling/field heating (FC/FH) at 1 kV/cm for $Sr_{1-1.5x}Bi_xTiO_3$ with $x=0.002$. The data were obtained form the measurement of hysteresis loop at 1 Hz.

dence of ϵ'' are in good agreement with the experimental data, as shown in the inset of Figs. 1 and 2.

The polarization data have been obtained from the measurement of hysteresis loops for the sample with $x=0.002$, at 1 Hz after zero-field cooling/field heating (ZFC/FH) and field cooling/field heating (FC/FH) at 1 kV/cm, with cooling and heating rates of 1 K/min. The temperature dependence of the polarization P is shown in Fig. 3. It can be seen that there are two clear steps of the polarization processes which correspond well to the modes A and B, respectively.[24] From Fig. 3, we can get $\triangle P_B=0.0011$ C/m^2 and $\triangle P_A=0.0008$ C/m^2. In terms of the simple picture of an isolated single dipoles, $p=q\delta/V$, (V is the volume in which a dipole is included. Here for $x=0.002$, $V=500V_{cell}$, V_{cell} is the volume of an unit cell), we obtain $\delta_B=0.68$ Å and $\delta_A=0.49$ Å. These results are in agreement with the data obtained from the Eq. (2).

However, considering that the equation $p=q\delta/V$ is based on the hypothesis that the dipoles are isolated. If the dipoles are cooperative (we know that is true), the δ value must be decreased. It could be concluded that the δ value obtained from $p=q\delta/V$ is an upper limit of the displacement of the off-center Bi ions. In addition, the δ value, obtained from the Eq. (2), $\triangle\epsilon=n(Nq\delta)^2/3k_BT\epsilon_0$, depends on what value N we take. In this work, we took $N=20$, perhaps, N should be higher than 20, i.e., the δ value might be smaller than the upper limit value obtained from the polarization calculation. If taking $N=100$, we obtain $\delta_B=0.14\pm0.02$ Å for mode B and $\delta_A=0.07\pm0.02$ Å for mode A. These data are near the displacement $\delta=\sim0.2$ Å calculated by Skanavi *et al.*[25] from an empirical estimation taking into account the enhancement of the internal electric field. At this stage, a firm theoretical basis for this enhancement factor N has not yet been established.

Raman spectra of Bi-doped ST at 50 K are shown in Fig. 4. At 50 K, for the nominally pure ST sample, the optical phonons at the R point of the Brillouin zone are at 20, 40, 54, 150, 178, 240, 270, 290, 450, and 550 cm^{-1}; these lines have been reported in the earlier literature.[26–28] The lines at 20, 54, 150, 240, and 450 cm^{-1} were attributed to the proper first-order modes, which are predicted by the group theoretical analysis for the tetragonal structure (the cell-doubled tetragonal $I4/mcm$) of ST.[26] The lines at 270 and 290 cm^{-1} were associated with the second-order bands;[27] and the lines at 40, 178, and 550 cm^{-1} were attributed to the modes induced by the unavoidable defects and impurities.[28]

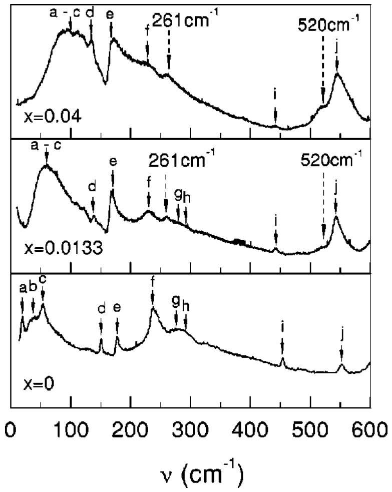

FIG. 4. Raman spectra for $Sr_{1-1.5x}Bi_xTiO_3$ with $x=0$, 0.0133, and 0.04 at 50 K. The lines at 20, 40, 54, 150, 178, 240, 270, 290, 450, and 550 cm^{-1}, are labeled as a, b, c, d, e, f, g, h, i, and j, respectively.

As seen from Fig. 4, with increasing Bi concentration, the lines at 20, 40, and 54 cm^{-1} merge into a rounded band and the line at 150 cm^{-1} remains. The lines at 240, 270, 290, and 450 cm^{-1} decrease with increasing Bi concentration, and almost disappear for $x=0.04$. The defect-induced modes at 178 and 550 cm^{-1} increase greatly with increasing Bi concentration. The results indicate that the phonons modes are greatly modulated by Bi doping. It is reasonable to assume that the change is due to distortion of the lattice structure induced by Bi doping. The results of x-ray diffraction indicated that all the samples are cubic. However, with a very careful inspection (at very slow scanning speed and small steps) we found that in addition to the distortion from Cu $K\alpha_1$ and Cu $K\alpha_2$, the splitting of the (200) peak becomes clearer with increasing Bi concentration, indicating that the samples become more distorted towards a ‘‘*tetragonal*’’ system. The great enhancement in the defect-induced modes (178 and 550 cm^{-1}) may reflect this distortion.

It should be emphasized that, for the Bi-doped samples, two new lines appear, one at ~261 cm^{-1} and another at ~520 cm^{-1}. Interestingly, these frequencies of the optical phonons at ~520 cm^{-1} (64.5 meV) and ~261 cm^{-1} (32.4 meV) are exactly coincided with the activation energies of mode B (62±2 meV) and mode A (33±1 meV) obtained from the dielectric relaxation. This result strongly suggests that the modes A and B are very probably related to the phonons of the host lattice of ST, i.e., the motion of the off-center Bi ions that contribute to the modes A and B could be correlated via the phonons interaction.[29] Obviously, this supports the enhancement effect of the effective polarization moment in Bi-doped ST.

Based on the above results, a simple picture can be drawn. For ST with deliberate Bi doping, off-center Bi ions form noninteracting polar clusters via the interaction with the phonons of the ST host lattice, giving rise to T_m-unshifted permittivity peaks with a single relaxation time that follows the Arrhenius law. These peaks are superimposed upon the background of the QPB of ST. The dielectric response could be described by the modified Debye-Langevin model. The present work indicates that a theoretical model should take into account of the possible coexistence of several different dielectric modes induced by the impurity. ST doped with very low concentration Bi ions behaves as a noninteracting polar clusters system.

With further increasing impurity concentration, some of the noninteracting clusters become interacting clusters, and these clusters contribute to a ferroelectric relaxor mode, whose relaxation time follows the Vogel-Fulcher law. When Bi concentration reaches a critical value, all the noninteracting clusters become interacting clusters, and only the relaxor behavior is present. This provides an example which shows an evolution of the ferroelectric relaxor mode and might be helpful in understanding the physical nature of the ferroelectric-relaxor behavior.

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*Present address: 187 Materials Research Laboratory, The Pennsylvania State University, University Park, PA 16802.

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