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BRIEF REPORTS

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Bi:SrTiO$_3$: A quantum ferroelectric and a relaxor

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Quantum ferroelectric and ferroelectric relaxor behavior has been found in $(\mathrm{Sr}_{1-1.5x}\mathrm{Bi}_x)\mathrm{TiO}_3$. For $x \leqslant 0.0267$, the quantum ferroelectric relationship $T_{\varepsilon_m} \propto (x - x_c)^{1/2}$ holds with $x_c \approx 0.0005$, and obvious hysteresis loops were observed. The polarization relaxation shows critical slowing down. At high Bi concentration, a crossover from quantum ferroelectric to relaxor behavior occurred. The coexistence of ferroelectric and relaxor behavior in Bi:SrTiO$_3$ was attributed to a ferroelectric domain state induced by random fields. [S0163-1829(98)02314-5]

Since the discovery of a family of materials, namely, ''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), which show a rounded permittivity peak and a low-frequency dispersion, the physical nature of the relaxors has been a challenging subject. On the other hand, similar relaxor behavior is also found in quantum paraelectric KTaO$_3$ doped with Li (KLT) (Refs. 4 and 5) or SrTiO$_3$ doped with Ca (SCT).[6,7] For example, both ferroelectric and dipole glass behavior was observed in KLT where a crossover from the dipole glass to a ferroelectric domain state occurred as the Li content increased.[8,9]

The two systems have been independently developed, and recently the common features were pointed out, mainly including (1) a large permittivity, (2) a low-frequency dispersion of permittivity and long relaxation time, (3) nonergodicity of permittivity,[10] (4) nanometer scale polar clusters,[11] and (5) compliance with both Vogel-Fulcher type[12] and de Almeida–Thouless type relationships.[10] It is recognized that the polar clusters, dipolar interaction, and random electric fields play a key role in the relaxors. However, different explanations were proposed for these observations. For example, for typical relaxor PMN, a ''dipolar glass'' model was suggested by Viehland *et al.*,[12] while a random-electric-field model was suggested also for PMN by Westphal *et al.*[13] Further studies are needed and a search for new systems is meaningful. Toulouse *et al.* pointed out that one of the obstacles in understanding the behavior of relaxors has been their complex structure and suggested that KLT with simple perovskite structure could be a model system for relaxors.[14] In this paper, the authors suggested that $(\mathrm{Sr}_{1-1.5x}\mathrm{Bi}_x)\mathrm{TiO}_3$ (SBT) could be a new model system for relaxors.

SBT exhibits a dielectric relaxation behavior, which was first reported by Skanavi *et al.*,[15,16] who attributed it to the mechanism of ''hopping ion'' polarization in the perovskite lattice absent of ferroelectricity. On the contrary, on the basis of slim electric hysteresis loops for SBT,[1,17] Smolenskii *et al.*[1] classified it as a ferroelectric relaxor similar to PMN. However, further studies either on the relaxor behavior or ferroelectric mechanisms in this system were not reported.

In this paper, we show that quantum ferroelectric behavior and the essential features of a ferroelectric relaxor were found in SBT and that a crossover from ferroelectric to relaxor behavior occurred with increasing Bi concentration.

The ceramic samples of $(\mathrm{Sr}_{1-1.5x}\mathrm{Bi}_x)\mathrm{TiO}_3$ $(0 \leqslant x \leqslant 0.167)$ were prepared by a solid-state reaction. The x-ray-diffraction results indicate that all the samples are single cubic phase, and energy dispersion analysis indicated that the Bi concentration is in agreement with the nominal composition, within the experimental error, and that the distribution of Bi atoms is uniform. Strontium vacancies V_{Sr} are created as $[\mathrm{Sr}_{1-1.5x}\mathrm{Bi}_x(\mathrm{Vs}_r)_{0.5x}]\mathrm{TiO}_3$, to balance the charge misfit due to the substitution of divalent Sr^{2+} ions by trivalent Bi^{3+} ions.[16,18] It was also shown that the dielectric permittivity was independent of the electrodes (three kinds of metals,

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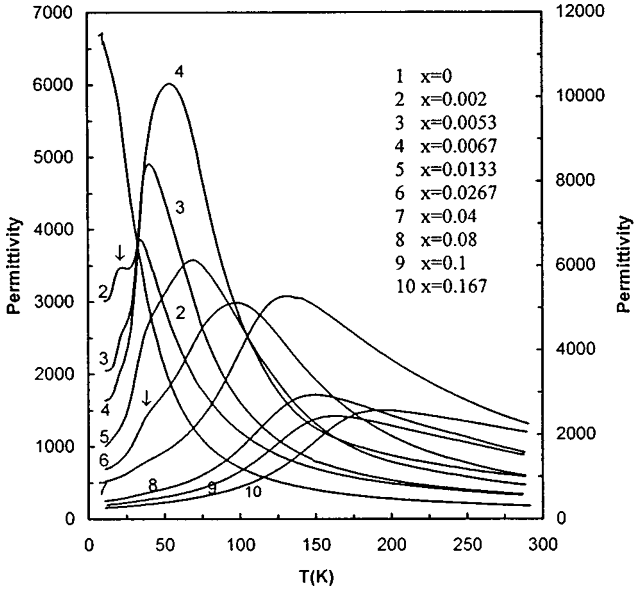

FIG. 1. Temperature dependence of the permittivity of $(Sr_{1-1.5x}Bi_x)TiO_3$ with x between 0 and 0.167 at 1 kHz (1, right scale; 2–10, left scale).

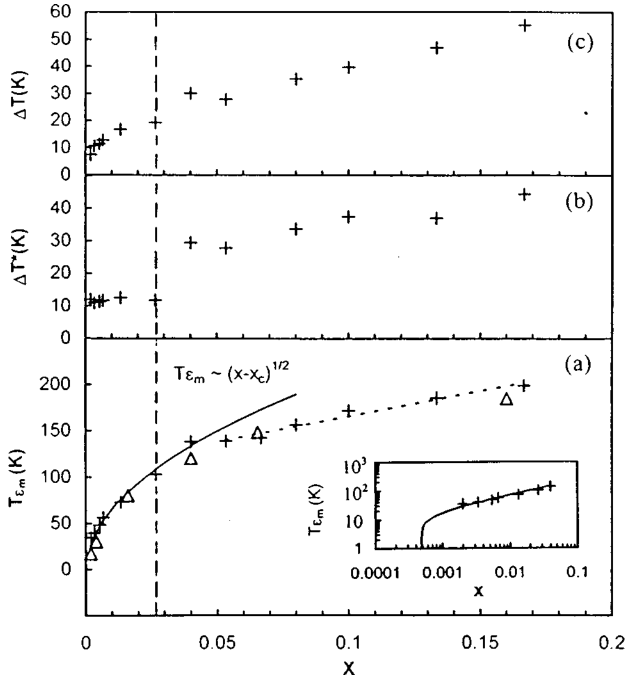

FIG. 3. (a) T_{ε_m} as a function of Bi concentration x at 1 kHz (+); the marks (Δ) are from Ref. 17, and the solid line corresponds to the $(x-x_c)^{1/2}$ law for QF behavior; the inset shows an enlarged T_{ε_m} vs x at the low x range with a log-log scale. (b) $\Delta T^* = T_{\varepsilon_m(100\,\mathrm{kHz})} - T_{\varepsilon_m(100\,\mathrm{Hz})}$ as a function of x. (c) $\Delta T = T_{0.9\varepsilon_m(100\,\mathrm{Hz})} - T_{\varepsilon_m(100\,\mathrm{Hz})}$ as a function of x.

silver, gold, and Pd-Ag alloy) and the thickness (disks, diameter 8 mm with thickness of 1 or 0.5 mm) of the samples. The dielectric complex permittivity was measured with a Solartron 1260 impedance gain-phase analyzer under an ac field of 1 V/mm. The hysteresis loops were measured using a standard Sawyer-Tower circuit.

Figure 1 shows the temperature dependence of the permittivity (ε) for all the samples at 1 kHz. Typical curves of ε as a function of temperature and frequency for the samples with $x=0.002$, 0.0133, and 0.08 are shown in Fig. 2. The results indicate that a permittivity peak occurred in SBT even with a very small amount of Bi $(x=0.002)$. Frequency dispersion was also observed, with the temperature of the permittivity maximum (T_{ε_m}) shifted to high temperatures with increasing frequency. The dielectric loss is in the range $\sim 0.001-0.01$ for all the samples at 300 K and 1 kHz, and the tendency of the temperature dependence is similar to that of the permittivity (not presented). Figure 3(a) shows the variation of T_{ε_m} versus Bi concentration at 1 kHz. T_{ε_m} increases with the bismuth content at different rates. The transition point occurs at bismuth content of about 0.0267. In the range of $0<x \leqslant 0.0267$, the T_{ε_m} as a function of Bi concentration can be well fitted to the equation[19] $T_{\varepsilon_m} \approx 670(x-x_c)^{1/2}$, with the quantum mechanical critical point $x_c = 0.0005 \pm 0.0001$, which is a typical relation for quantum ferroelectric (QF) behavior. On the other hand, for $x>0.0267$, a near linear increase of T_{ε_m} with x was observed, which is similar to the behavior of ferroelectric solid solutions.

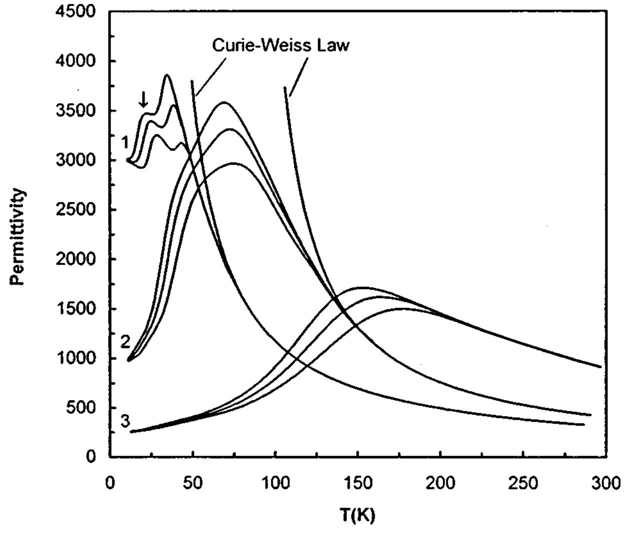

FIG. 2. Temperature and frequency dependence of the permittivity of $(Sr_{1-1.5x}Bi_x)TiO_3$ with x; 1, $x=0.002$; 2, $x=0.0133$; and 3, $x=0.08$ (1, 10, and 100 kHz, from top to bottom).

The relaxation time for the polarization derived from the temperature dependence of the imaginary parts of the permittivity for $x=0.0267$ is plotted in Fig. 4. The data were fitted to several equations, such as the Arrhenius relation, the Vogel-Fulcher law,[20] and the critical slow down relation.[21] The best fitting, with physically reasonable parameters, was obtained from the critical slow down relation.

$$\tau = h/k_B(T-T_0)^{-1} \exp[U/k_BT],$$

where h is Planck's constant and k_B is Boltzmann's constant, with activation energy $U=0.103$ eV and $T_0=69.9$ K. With the increase in Bi concentration, the parameters U and T_0 increased.

Conventional hysteresis loops have been observed in the present work. Figure 5 shows the hysteresis loops for several samples with applied ac fields up to $\sim 15\ \mathrm{kV\,m^{-1}}$ at 50 Hz.

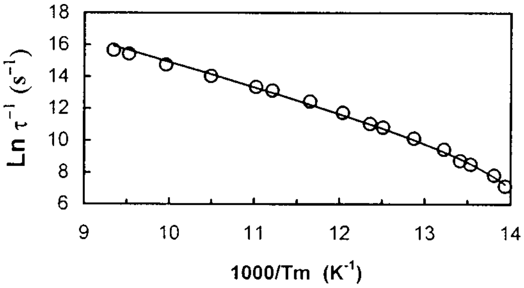

FIG. 4. Temperature dependence of the relaxation times τ ($\tau=\omega^{-1}$; ω is an angular frequency, and T_m is the temperature at which the maximum of the imaginary part of the permittivity at ω occurred) of $(\mathrm{Sr}_{1-1.5x}\mathrm{Bi}_x)\mathrm{TiO}_3$ with $x=0.0267$ (dots, the experimental data; the solid line, fitting to the critical slowing-down relation).

The remnant polarization is 0.31 μC/cm^2 for $x=0.0033$, 0.83 μC/cm^2 for $x=0.0133$, and 0.32 μC/cm^2 for $x=0.0533$. These values are higher than those of SCT,[22] but much smaller than those of the normal ferroelectric, such as BaTiO_3.[21] From Fig. 5, it can be seen that the low Bi compositions, for which the quantum ferroelectric equation $T_{\varepsilon_m}\sim(x-x_c)^{1/2}$ holds, exhibit an obvious hysteresis loop with high polarization values; when the Bi content exceeds this range ($x=0.0267$), the hysteresis loop becomes slim.

The temperature dependence of the permittivity (at 100 kHz) for all the samples was fitted to the Curie-Weiss law in the high-temperature side. For the sample with $x=0$, the fitting parameter, Curie-Weiss constant $C=0.81\times10^5$, Curie-Weiss temperature $\Theta=33.3$ K are in reasonable agreement with the parameters $C=0.8\times10^5$ and $\Theta=35.5$ K, reported by Müller and Burkhard.[23] For the doped samples, obvious deviations from Curie-Weiss behavior on the high-temperature side of the permittivity peaks were observed, as shown in Fig. 2 where typical curves are presented. Similar deviations were observed in other relaxor systems, such as PMN (Ref. 24) and $(\mathrm{Ca}_x\mathrm{Sr}_{1-x})\mathrm{TiO}_3$ (SCT).[22] The deviation from the Curie-Weiss law on the high-temperature side was explained as an indication of the existence of fluctuations of the polar regions around T_{ε_m}. The frequency dispersion of permittivity and an obvious departure from the Curie-Weiss law observed in Fig. 2 suggest for SBT a relaxor-type behavior. The diffuseness of the phase transition can be described by an empirical parameter ΔT, defined as the difference between $T_{0.9\varepsilon_m(100\,\mathrm{Hz})}$ [the temperature corresponding to 90% of the permittivity maximum (ε_m) on the high-temperature side] and $T_{\varepsilon_m(100\,\mathrm{Hz})}$, i.e., $\Delta T=T_{0.9\varepsilon_m(100\,\mathrm{Hz})}-T_{\varepsilon_m(100\,\mathrm{Hz})}$. Another parameter ΔT^* adopted to quantify the degree of relaxation behavior is defined as $\Delta T^*=T_{\varepsilon_m(100\,\mathrm{kHz})}-T_{\varepsilon_m(100\,\mathrm{Hz})}$. The ΔT and ΔT^* parameters obtained are illustrated in Figs. 3(b) and 3(c). It can be seen that, for the samples with low x, both values are small, implying close to normal ferroelectric behavior. With an increase in Bi content, the two parameters increase quickly, implying that the system is becoming more relaxor.

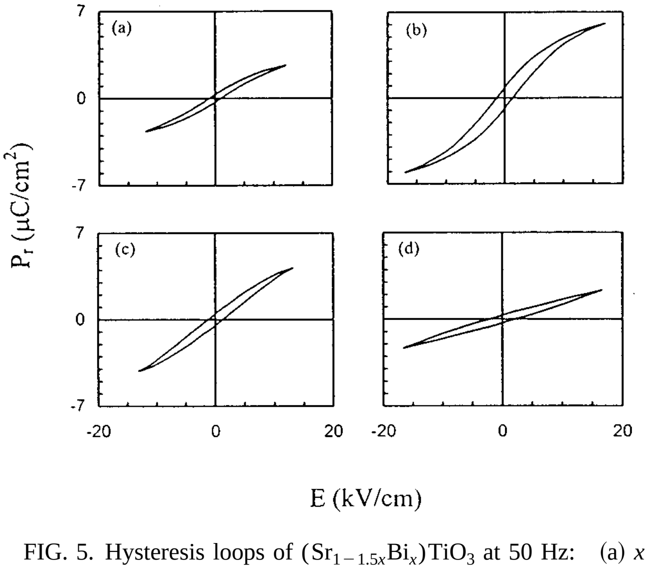

FIG. 5. Hysteresis loops of $(\mathrm{Sr}_{1-1.5x}\mathrm{Bi}_x)\mathrm{TiO}_3$ at 50 Hz: (a) $x=0.0033$ at 11 K, (b) $x=0.0067$ at 11 K, (c) $x=0.0133$ at 11 K, and (d) $x=0.0533$ at 80 K.

The existence for the low Bi content samples of a large permittivity peak, the good fitting to the critical slowing-down relation with physically reasonable physical sense for the equation parameters, the good fitting to the relation $T_{\varepsilon_m}\sim(x-x_c)^{1/2}$, indicative of quantum ferroelectric behavior, and the obvious hysteresis loops observed give strong evidence for a ferroelectric state caused by doping SrTiO_3 with Bi. For higher-Bi-content samples, the existence of a rounded permittivity peak and of frequency dispersion behavior and the obvious departure from the Curie-Weiss law point to relaxor behavior.

In SCT, Bednorz and Müller[6] observed the occurrence of a permittivity peak and a crossover from the XY quantum ferroelectric state, with a sharp permittivity peak, to one with a ''diffusive character'' as the Ca content increased.[6] 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. Comparing SBT with SCT, several similarities can be found: (1) Both Ca and Bi ions substitute into the Sr^{2+} sites; for Bi, $r_{\mathrm{Bi}}^{3+}/r_{\mathrm{Sr}}^{2+}$ is 0.87, and for Ca, $r_{\mathrm{Ca}}^{2+}/r_{\mathrm{Sr}}^{2+}$ is 0.85. (2) Both Ca and Bi doping lead to the occurrence of a permittivity peak, even for a very small amount of the dopant. (3) A similar concentration dependence of T_{ε_m} was obtained in both cases; for low Ca or Bi content, a quantum ferroelectric relationship holds.

It was hypothesized that a decrease in repulsive forces and an increase in polarization forces, for an impurity ion relative to the lattice ion it replaces, favor off-center positioning.[9] Then the Bi ion with smaller size and high polarizability may also be located in off-center positions at the Sr^{2+} sites. In addition, the appearance of strontium vacancies V_{Sr} to balance the charge misfit due to the substitution of divalent Sr^{2+} ions by trivalent Bi^{3+} ions might lead to the formation of the associate defects Bi^{3+}-V_{Sr}. Such off-center Bi ions and Bi^{3+}-V_{Sr} centers will form dipoles and thus set up local electric fields and/or strain fields. The SBT system will then be a random-site electric dipole system, with the off-center Bi and/or (Bi^{3+}-V_{Sr}) dipoles randomly distributed in the highly polarizable host lattice of SrTiO_3, and in this way it is then similar to SCT. The appearance of ferroelectric and relaxor behavior can result from competition of the interaction of dipoles and random electric and/or strain fields.

However, some experimental facts differ from the well-known relaxors PMN, PST, KLT, and SCT. Comparing with the compounds PMN and PST, SBT is a solid solution with simple perovskite structure, and since its ''relaxation degree'' can be adjusted by the Bi concentration, it takes an advantage for fundamental research. For SCT, SBT provided a comparative system. For example, Bi doping makes a monotonic increase in T_c until $x=0.167$, while, for SCT, T_c is independent of Ca concentration as $x \geqslant 0.016$,[6] and for SCT, $T_c \approx 298(x-0.0018)^{1/2}$;[6] for SBT, $T_c \approx 670(x-0.0005)^{1/2}$ was obtained. This means that Bi doping makes T_c increase about 2 times faster than Ca in SCT. In addition, Bednorz and Müller[6] reported that no obvious frequency dispersion behavior was observed in SCT. However, in SBT, all samples showed diffuse transitions and frequency dispersion, and these tendencies increased with increasing Bi concentration. These differences probably are due to the heterovalent substitution and A-site vacancies in SBT. The reasons should be further studied.

Another character of SBT is the existence of Sr-site vacancies in SBT.[16,18] A-site vacancies in perovskite ABO_3, making a more rounded permittivity peak appearance, were also found in the PST ferroelectric relaxor when Pb-site vacancies were present.[25] The present authors suppose that the similarity between SBT and SCT and the differences could provide a model system to explore further the effect of the A-site vacancies and heterovalent substitution on the ferroelectric relaxor behavior.

Besides, some special interesting features of SBT are that (1) the oxygen content of SBT could be controlled by annealing in different atmospheres due to the existence of A-site vacancies.[18] It was found that T_c shifts to high temperature and the vibration frequency of the crystal lattice increases by increasing oxygen content.[18] This implies that it will be possible to study the relation between T_c and the vibration frequency of the crystal lattice in SBT. (2) In SBT, for low Bi concentration, in addition to the ε peak discussed above, there are two other peaks of permittivity below 40 K (indicated by arrows in Figs. 1 and 2). They are also rounded and frequency dependent, but its T_{ε_m} is independent of the Bi concentration and oxygen content. They might be related to the coherent quantum state of $SrTiO_3$ below 37 K, suggested by Müller *et al.*,[26] or the effect of Bi coupling with the soft mode of $SrTiO_3$. The origin of this peak needs further study.

In conclusion, we have (1) demonstrated that SBT is a quantum ferroelectric for $x \leqslant 0.0267$, (2) shown that a critical slowing-down behavior was observed, (3) shown that remanent polarization obtained from hysteresis loops varied with Bi concentration, and (4) shown that with increasing Bi concentration, a crossover from the quantum ferroelectric to ferroelectric relaxor state occurred. The coexistence of quantum ferroelectric behavior and ''relaxor'' behavior can be attributed to a ferroelectric domain state induced by random fields. Some specialties of SBT, for example, a very small $x_c(\sim 0.0005)$, the effect of the Sr-site vacancy, the relation between T_c and the oxygen vacancy, and the dielectric anomalies below 40 K, are also presented. SBT has a simple perovskite structure with the Sr-site vacancies and displays a varied interesting behavior. The authors suggested that SBT could be a possible model system to further understand the physical nature of ferroelectric relaxors or the quantum paraelectric matrix doped with dipolar impurities.

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