Impurity-induced ferroelectric relaxor behavior in quantum paraelectric SrTiO$_3$ and ferroelectric BaTiO$_3$

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We report that ''ferroelectric relaxor'' behavior is induced by doping Bi in quantum paraelectric SrTiO$_3$, and doping Ce in typical ferroelectric BaTiO$_3$. The present results show that the ''ferroelectric relaxor'' state may exist no matter whether the matrix is ferroelectric or paraelectric, however, the relaxor behavior is the dynamic response of the polar clusters induced in the system.

I. INTRODUCTION

The ''ferroelectric relaxor'' behavior, which shows a rounded permittivity peak with low-frequency dispersion, was first observed by Smolenskii *et al.* in the Ba(Ti,Sn)O$_3$ solid solution in 1954.[1] Later, this phenomenon was also observed in Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (PMN) compounds by the same group.[2] Smolenskii *et al.* named this phenomenon as a behavior of the ferroelectric with diffuse phase transition (DPT).[3]

In the earlier studies during the 1960's and 1970's, Smolenskii *et al.* proposed that the compositional heterogeneity (or compositional fluctuation) on the cation site was responsible for DPT.[3] However the model of Smolenskii *et al.* cannot explain why the temperature of the permittivity maximum increases with increasing frequency. In 1980, Setter and Cross reported the influence of order-disorder transitions on the relaxor behavior of Pb(Sc$_{1/2}$Ta$_{1/2}$)O$_3$.[4] In 1983, Yao, Chen, and Cross suggested that the microdomains play an essential role in ''ferroelectric relaxors,'' based on the observation of the microdomain to macrodomain switching, which was corresponding to the relaxor-normal ferroelectric transition in the (Pb,La)(Zr,Ti)O$_3$.[5] In 1987, Cross proposed that the nanometer-scale polar regions in relaxors were dynamic in nature with the dipole moment thermally fluctuating between equivalent directions, and the ferroelectric relaxors were, in some way, electrical analogues of the superparamagnets, the so-called superparaelectrics.[6] Later, a modified model, i.e., the ''dipolar-glass'' model, was proposed for the ferroelectric relaxors by Viehland *et al.*[7] In this model, the correlation between polar clusters was taken into account in analogy to the spin-glass systems.[7] Meanwhile, Westphal *et al.*[8] attributed the rounded permittivity peaks with frequency dispersion in PMN to the presence of domain states induced by quenched random fields. They argued that the ground state of the PMN might be ferroelectric, and the random fields induced by the compositional fluctuation lead to the occurrence of domain states.

A question has been raised, ''Is the ferroelectric relaxor behavior relevant to whether the ground state of materials is ferroelectric or paraelectric?''

On the other hand, although the relaxor behavior was first observed in BaTiO$_3$ related solid solutions, the main work for relaxor is focused on the Pb-based complex compounds. Great effort has been devoted to understand the physical nature of the ''ferroelectric relaxors.''[1–18] However, full understanding has not been reached so far. Recently, Toulouse *et al.* pointed out that one of the obstacles in understanding the behavior of the relaxors has been their complex structure, and they suggested that Li-doped quantum paraelectric KTaO$_3$ (KLT) could be a model system for ''ferroelectric relaxors,''[18] due to the ''ferroelectric relaxor'' behavior and the simple perovskite structure of KLT.

In the present paper, the polarization and dielectric behavior of Bi-doped quantum paraelectric SrTiO$_3$ and Ce-doped ferroelectric BaTiO$_3$ were studied. The results show that both systems with simple cubic perovskite structure display the typical ''ferroelectric relaxor.''

II. EXPERIMENTAL PROCEDURE

The ceramic samples of (Sr$_{1-1.5x}$Bi$_x$)TiO$_3$ (x = 0.0533, 0.1, and 0.2) and Ba(Ti$_{1-y}$Ce$_y$)O$_3$ (y = 0.06, 0.1, and 0.2) were prepared by the solid state reaction. The x-ray diffraction results indicate that all the samples are single cubic phase at room temperature. Dielectric complex-permittivity was measured with an HP 4284A meter in the frequency range 20 Hz to 1 MHz under the ac field of 1 V/mm. The temperature dependence of dielectric properties was measured in a cryostat system from 11 to 300 K, and in a furnace for higher temperatures, while the temperature of the specimen was being cooled or heated up at a rate of 1 K per minute and readings were taken every 1 K or 2 K.

III. RESULTS AND DISCUSSION

A. ''Ferroelectric relaxor'' behavior induced by doping in paraelectric SrTiO$_3$

The temperature dependence of the real and imaginary parts of the permittivity (ϵ' and ϵ'') for the (Sr$_{1-1.5x}$Bi$_x$)TiO$_3$ (x = 0.0533, 0.1, and 0.2) samples at 0.1, 1, 10, and 100 kHz is shown in Fig. 1. Rounded ϵ' peaks
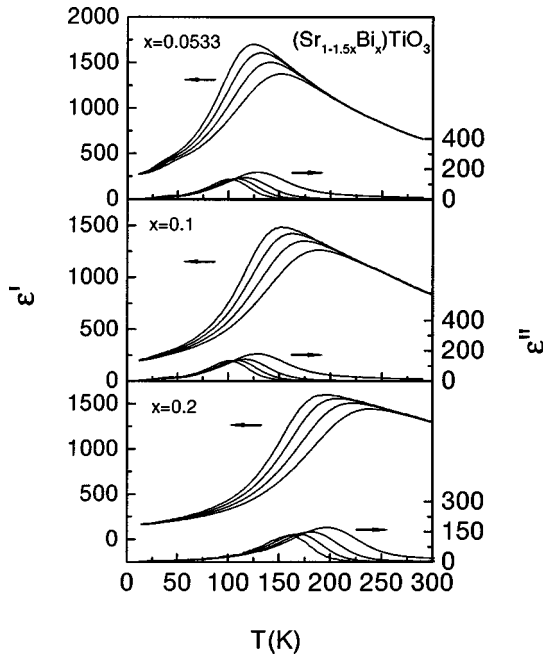
FIG. 1. Temperature dependence of the real and imaginary parts of the permittivity (ϵ' and ϵ'') for the $(Sr_{1-1.5x}Bi_x)TiO_3$ ($x = 0.0533$, 0.1, and 0.2) samples at 0.1, 1, 10, and 100 kHz (from top to bottom for ϵ', from left to right for ϵ'', respectively).

occur for all samples, the temperature (T_m) of ϵ'' maximum increases with increasing frequency, and T_m increases with increasing Bi.

The relaxational times τ for these sets of peaks were obtained from the frequency dependence of the imaginary part of the permittivity, and it is found that τ follows the Vogel-Fulcher law,[19] $\tau = \tau_0 \exp[U/k_B(T-T_{VF})]$, rather than the Arrhenius law. The curves are shown in Fig. 2. The fit parameters, for example, as $x = 0.0533$, $\tau_0 = 4.26 \times 10^{-9}$ s, $T_{VF} = 75$ K were obtained; the data for all samples are shown in Table I.

Conventional hysteresis loops have been measured by using standard Sawyer-Tawer circuit. Hysteresis loops for $x = 0.0533$ at different temperatures and at 50 Hz with electric fields lower than 20 kV cm^{-1} are shown in Fig. 3(a). At 11 K, the remanent polarization of 0.83 μC/cm^2 was obtained. This value is about one order of magnitude higher than that of Ca-doped SrTiO$_3$,[20] and much smaller than that of the normal ferroelectric BaTiO$_3$.[21] The remanent polarization P_r is shown in Fig. 3(b).

B. ''Ferroelectric relaxor'' behavior induced by doping in ferroelectric BaTiO$_3$

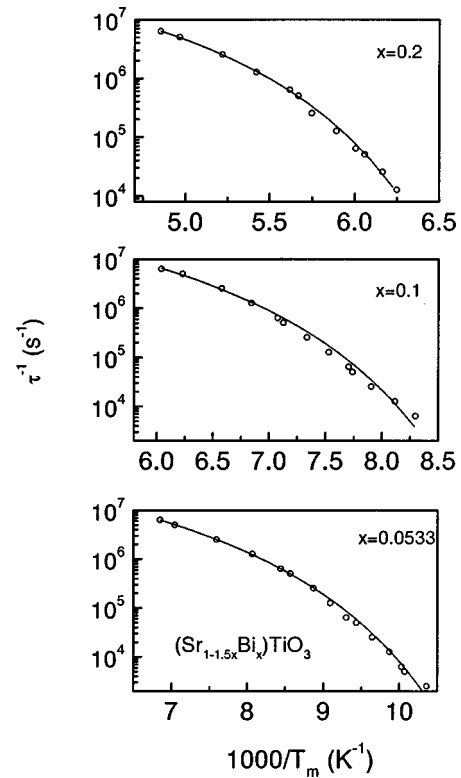The temperature dependence of the ϵ' and ϵ'' of Ba(Ti$_{1-y}$Ce$_y$)O$_3$ ($y = 0.06$, 0.1, and 0.2) ceramic samples in

FIG. 2. Relaxation time τ vs $1/T_m$ curve for $(Sr_{1-1.5x}Bi_x)TiO_3$ ($x = 0.0533$, 0.1, and 0.2) (open circles, the experimental data; solid curves, fits to the Vogel-Fulcher law).

the temperature range of 11–500 K at 1, 10, and 100 kHz is shown in Fig. 4. Compared with the three sharp phase transitions at 383 K, 285 K, and 204 K in nominally pure BaTiO$_3$ (not shown here), the three permittivity peaks merge into one permittivity peak for all the Ba(Ti$_{1-y}$Ce$_y$)O$_3$ ($y = 0.06$, 0.1, and 0.2) samples, as shown in Fig. 4. This dielectric peak is remarkably rounded with frequency dispersion. For Ba(Ti$_{1-y}$,Ce$_y$)O$_3$, as $y = 0.06$, it should be emphasized that although the frequency dispersion and relaxation behavior is small, i.e., the increment ΔT of the T_m (the temperature of the permittivity maximum) is 1.4 K as the frequency increases from 100 Hz to 100 kHz, the corresponding relaxation time τ follows the Vogel-Fulcher law. For $y = 0.1$ and 0.2, the ΔT increases, and the relaxation times τ also follow the Vogel-Fulcher law. The fit curves are shown in Fig. 5, and the fit parameters are listed in Table I. The hysteresis loops of the Ba(Ti$_{0.8}$Ce$_{0.2}$)O$_3$ measured at different temperatures are shown in Fig. 6(a). At 160 K, a hysteresis loop, with a maximum loop area, was observed. With increasing temperature, a slimmer hysteresis loop can be found in the Ba(Ti$_{0.8}$Ce$_{0.2}$)O$_3$ sample. The saturation polar-

TABLE I. The activation energy, preterm, and characteristic temperature of the Vogel-Fulcher relation for the Ba(Ti$_{1-y}$Ce$_y$)O$_3$ ($y = 0.06$, 0.1, and 0.2) and $(Sr_{1-1.5x}Bi_x)TiO_3$ ($x = 0.0533$, 0.1, and 0.2) solid solutions.

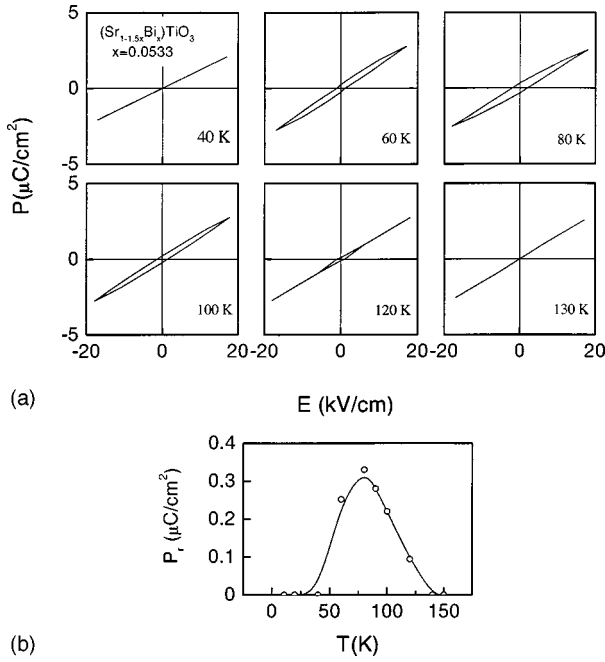|	Ba(Ti$_{1-y}$Ce$_y$)O$_3$			$(Sr_{1-1.5x}Bi_x)TiO_3$		
x,y	0.06	0.1	0.2	0.0533	0.1	0.2
τ_0 (s)	6.91×10^{-12}	6.91×10^{-12}	9.24×10^{-9}	4.26×10^{-9}	2.43×10^{-9}	3.25×10^{-9}
E (meV)	3.9	7.6	27	22	25	25
T$_{VF}$	347 K	320 K	139 K	75 K	95.5 K	132 K

FIG. 3. (a) Hysteresis loops at different temperatures of $(Sr_{1-1.5x}Bi_x)TiO_3$ for $x=0.0533$ at 50 Hz. (b) Temperature dependence of the remanent polarization P_r.

ization is dependent on the temperature, being 3.3 $\mu C/cm^2$, with a coercive field 1 kV/cm, at 160 K. Remanent polarization (P_r) as a function of temperature derived from the hysteresis loop measurements is shown in Fig. 6(b). At temperatures lower than 50 K, the P_r is nearly zero. When temperature is higher than 50 K, the P_r first increases with increase in temperature, until a maximum at about 160 K, and then it decreases with further increase in temperature. However, it does not go to zero at permittivity maximum temperature ($T\epsilon_m$), but inflects and tails to zero, which shows a typical relaxor characteristic.

C. The characterization of the ''ferroelectric relaxor'' behavior

The results indicate that both $(Sr,Bi)TiO_3$ and $Ba(Ti,Ce)O_3$ display a ferroelectric relaxor behavior, especially for high impurity doping, for example, for $x,y=0.1$ and 0.2. In order to characterize the dielectric dispersion and diffuseness of the doped systems, an empirical expression was proposed:[22,23]
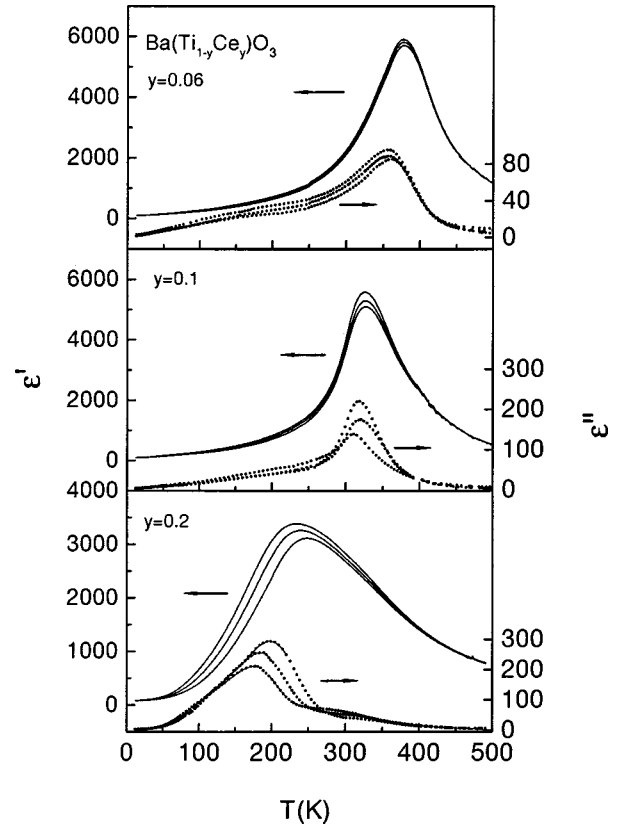
$$1/\epsilon - 1/\epsilon_m = (T-T_m)^\gamma/C, \qquad (1)$$

FIG. 4. Temperature dependence of the real and imaginary parts of the permittivity (ϵ' and ϵ'') for the $Ba(Ti_{1-y}Ce_y)O_3$ ($y=0.06$, 0.1, and 0.2) samples at 1, 10, and 100 kHz (from top to bottom for ϵ', from left to right for ϵ'', respectively).

where γ and C are assumed to be constant with $1 \leq \gamma \leq 2$. The limiting values $\gamma=1$ and $\gamma=2$ reduce the expression to the Curie-Weiss law valid for the case of a normal ferroelectric and to the quadratic dependence valid for an ideal relaxor, respectively. The diffuseness of the phase transition can be described by an empirical parameter $\Delta T_{diffuse}$, defined as

$$\Delta T_{diffuse} = T_{0.9\epsilon_{m(100\ Hz)}} - T\epsilon_{m(100\ Hz)}, \qquad (2)$$

i.e., the difference between $T_{0.9\epsilon_{m(100\ Hz)}}$ [the temperature corresponding to 90% of the permittivity maximum (ϵ_m) in the high-temperature side] and $T_{m(100\ Hz)}$.

On the other hand, the degree of relaxation behavior can be described by a parameter $\Delta T_{relaxor}$, which is defined as[22,23]

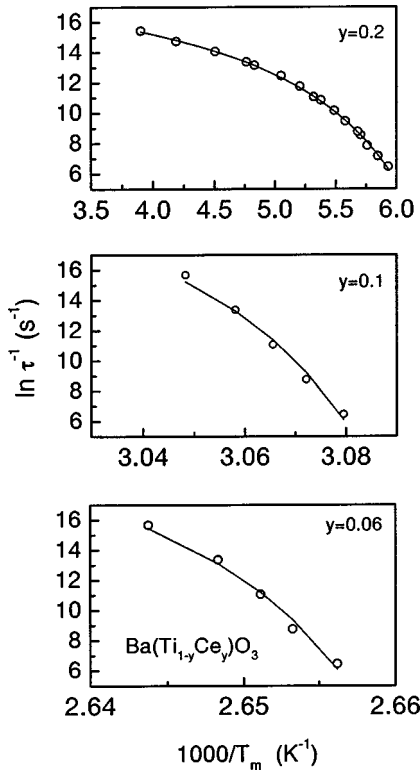$$\Delta T_{relaxor} = T_{m\ (100\ kHz)} - T_{m\ (100\ Hz)}. \qquad (3)$$

TABLE II. The $T\epsilon_m$, γ, ΔT_{relax}, and $\Delta T_{diffuse}$ for the $Ba(Ti_{1-y}Ce_y)O_3$ ($y=0.06$, 0.1, and 0.2) and $(Sr_{1-1.5x}Bi_x)TiO_3$ ($x=0.0533$, 0.1, and 0.2) solid solutions.

	$Ba(Ti_{1-y}Ce_y)O_3$			$(Sr_{1-1.5x}Bi_x)TiO_3$		
x,y	0.06	0.1	0.2	0.0533	0.1	0.2
$T\epsilon_m$ (100 kHz)	377 K	326 K	240 K	153.4 K	190.9 K	238.9 K
γ (10 kHz)	1.83	1.46	1.7	1.69	1.56	1.64
$\Delta T_{diffuse}$ (100 Hz)	20 K	20.5 K	44.5 K	27.8 K	39.7 K	41.4 K
ΔT_{relax}	1.4 K	1.6 K	15.8 K	27.8 K	37.5 K	47.5 K

FIG. 5. Relaxation time τ vs $1/T_m$ curve for $Ba(Ti_{1-y}Ce_y)O_3$ ($y=0.06$, 0.1, and 0.2) (open circles, the experimental data; solid curves, fits to the Vogel-Fulcher law).

The fit data of γ, $\Delta T_{diffuse}$ and $\Delta T_{relaxor}$ obtained for all the samples are presented in Table II. This indicates that the dielectric dispersion and diffuseness of both $(Sr,Bi)TiO_3$ and $Ba(Ti,Ce)O_3$ are qualitatively similar. With increasing Bi or Ce doping concentration, the degree of the diffuseness and relaxation of the solid solutions increases.

D. Discussion

For ''ferroelectric relaxor'' there are numerous reports showing that the relaxation time follows the empirical Vogel-Fulcher law rather than the Arrhenius law. Although the explanation of the empirical Vogel-Fulcher law is still uncertain,[7,24,25] the relaxation time τ following the Vogel-Fulcher law is one of the characteristics of the ''ferroelectric relaxor.''

In the present work, we have observed the rounded permittivity peaks with frequency dispersion, the T_m being shifted to higher temperatures with increasing frequency, the relaxation time following the Vogel-Fulcher law, the slim hysteresis loops, and the bell-like profile of the P_r vs T curves in both $(Sr,Bi)TiO_3$ and $Ba(Ti,Ce)O_3$. This confirms that both $(Sr,Bi)TiO_3$ and $Ba(Ti,Ce)O_3$ exhibit a ''ferroelectric relaxor'' behavior. This indicates that the ferroelectric relaxor behavior could be induced by doping impurity in both quantum paraelectric and typical ferroelectric.

It is recognized that the Bi impurity in $SrTiO_3$ occupies at an off-center position at Sr sites, and these off-center Bi ions form the dipoles.[26,27] With increasing Bi concentration, the
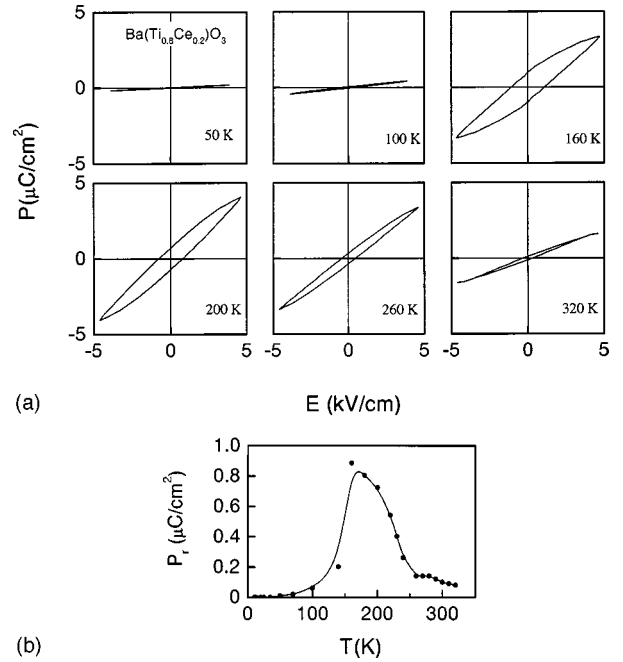

(a)

(b)

FIG. 6. (a) Hysteresis loops at different temperatures of $Ba(Ti_{1-y}Ce_y)O_3$ for $y=0.2$ at 50 Hz. (b) Temperature dependence of the remanent polarization P_r.

dipoles form micropolar clusters in the doped system, which contribute to the ''ferroelectric relaxor'' behavior. It can be also conjectured that if a proper condition existed, the system would become a conventional ferroelectric. However, no sharp ferroelectric transition is observed in $(Sr,Bi)TiO_3$, this might be due to that defects, such as hetrovalence Bi substitution, Sr-sites vacancies, and oxygen vacancies in the samples may result in high local random fields, which block the long-range order occurring.

The $Ba(Ti,Ce)O_3$ can be considered as the solid solution of $BaTiO_3$ and $BaCeO_3$, and both Ti and Ce ions occupy at the B sites of ABO_3 perovskite structure. It is known that the $BaCeO_3$ is nonferroelectric. Based on the concept of the ''active Ti ions'' proposed by Slater,[28] Ce is at central position with no displacement. In this case, the macrodomains in pure $BaTiO_3$ are divided into microdomains by some contents of Ce ions doping, and the domain state appears.[29]

IV. CONCLUSION

In conclusion, we have observed that the ''ferroelectric relaxor'' behavior can be induced in both the quantum paraelectric and the typical ferroelectric. This indicates that the ''ferroelectric relaxor'' is not directly related to whether the matrix is paraelectric or ferroelectric, however, it is closely related to the appearance of the micropolar clusters in the system. The behavior arises from the dynamic response of the micropolar clusters, which exist in the off-center ions doped paraelectric or some ions doped ferroelectric. This provides composition-controlled systems for studying the physical nature of the ''ferroelectric relaxor'' with simple cubic perovskite structure.

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