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Study of $Ba_xSr_{1-x}TiO_3$ thin films using transverse-field Ising model

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In this paper, the effects of doping on the thermodynamic properties of $Ba_xSr_{1-x}TiO_3$ (BST) thin film are investigated, based on the transverse-field Ising model (TIM) within the framework of mean field theory. We apply the double-peak distribution model of related parameters to mimic doping. The lattice expansion arising from doping with large Ba^{2+} was also taken into account. We concentrate on the doping concentration dependence of peak temperature (T_m), spontaneous polarization and dielectric susceptibility. It is found that the doping concentration has great influence on the dielectric properties and phase transition properties of BST thin films. We also discuss the quantum effect arising from doping.

Keywords: BST thin films, critical behaviour, TIM
PACC: 7720, 7755, 7780B

1. Introduction

(Ba,Sr)TiO_3 (BST) thin film is the dielectric material of choice for the next-generation dynamic random access memories (DRAMs) having gigabit densities, such as 1 and 4Gb DRAMs.[1,2] Various experimental methods such as film deposition, sputtering, x-ray, etc, make this novel material possible.[3] But its ferroelectric and dielectric properties require further research.[4] Strontium titanate ($SrTiO_3$) is known as an intrinsic quantum paraelectric [5,6] which shows very high dielectric permittivity at low temperature and no ferroelectric phase transition occurs as the temperature goes down to almost 0K.[7–9] However, being a highly polarizable state, the quantum paraelectric state can be destroyed by small perturbations from the external electric field or impurities and deduce a polar state. Barium titanate ($BaTiO_3$) is a typical ferroelectric material, which exhibits three sharp transitions: a first-order ferroelectric–paraelectric phase transition (cubic–tetragonal) around 130°C, a tetragonal–orthorhombic phase transition around 5°C and an orthorhombic–rhombohedral phase transition around −80°C.[5,8] In $Ba_xSr_{1-x}TiO_3$ the quantum paraelectric behaviour and ferroelectric behaviour are competing with each other, so that the BST system exhibits many interesting characteristics. There exists a critical concentration x_c, which separates the phase behaviour into two regions, one is $SrTiO_3$-like quantum paraelectric phase transition ($x < x_c$) and the other is $BaTiO_3$-like ferroelectric phase transition ($x > x_c$).[10–13] And there is another critical concentration x_{c1} between x_c and 1, which separates the first-order phase transition and the second-order transition.

In our present paper, the behaviours of $Ba_xSr_{1-x}TiO_3$ thin films are investigated under a mean-field approximation within the framework of the transverse-field Ising model (TIM). We suppose the distribution of the J, Ω, μ to be homogeneous and apply the double-peak distribution model of related parameters to this doped system. The lattice expansion, due to doping with large Ba^{2+}, is taken into account by a linear Vegard law.[13,14] We concentrate on the doping concentration dependence of spontaneous polarization, dielectric susceptibility, peak temperature (T_m) and hysteresis loops. We find that the doping concentration has great influence on the dielectric properties and phase transition properties of BST thin films. The quantum effect arising from doping is also investigated.

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2. Theory

Within the framework of the TIM, the Hamiltonian for ferroelectrics is given by

$$H = -\Omega\sum_i S_i^x - \frac{1}{2}\sum_{ij} J_{ij}S_i^zS_j^z - \frac{1}{4}\sum_{ijkl} J_{ijkl}S_i^zS_j^zS_k^zS_l^z - 2\mu E\sum_i S_i^z, \quad (1)$$

where $i \neq j$, Ω is the tunnelling frequency, μ is the dipole moment on single ion and E is the external electric field. S_i^x and S_i^z are the x and z components of pseudo-spin ($S = 1/2$) in the ith site, and J_{ij} and J_{ijkl} are the two-spin and four-spin interaction coupling constants, respectively.

Undoubtedly, most previous works have already shown that TIM is not only generally believed to be a good description for ferroelectric system but also successfully describes the quantum paraelectric system.[15,16] When the transverse field is less than the critical value $\Omega_c(2\Omega_c = ZJ)$, the system changes from paraelectric phase to ferroelectric phase as the temperature deviation $(T - T_c)$ changes from positive to negative. When $\Omega > \Omega_c$, spontaneous polarization does not appear even at T=0K and dielectric susceptibility saturates in low temperature. Its susceptibility function, consisting with the well-known Barrett formula,[17] describes the large quantum fluctuation behaviour of the quantum paraelectric well. In addition, in TIM the four-body interactions determine the properties of phase transition. When $\widetilde{J}' > 4\widetilde{J}/3$ $\left(\widetilde{J}' = \sum_{jkl} J_{ijkl}, \widetilde{J} = \sum_j J_{ij}\right)$, the first-order phase transition occurs. Otherwise, the second-order phase transition occurs.[18,19]

In this paper we are interested in $Ba_xSr_{1-x}TiO_3$ thin films. As we pointed out in the Introduction, the doping concentration of Ba^{2+} plays an important role in properties of BST thin films. How to consider the effect of doping in BST thin films is our first task to deal with. Here we apply the double-peak distribution model of related parameters to account for them. The distribution function can be expressed as follows:

$$\begin{aligned} P(J) &= x\delta(J - J_1) + (1 - x)\delta(J - J_2), \\ P(\Omega) &= x\delta(\Omega - \Omega_1) + (1 - x)\delta(\Omega - \Omega_2), \\ P(\mu) &= x\delta(\mu - \mu_1) + (1 - x)\delta(\mu - \mu_2), \end{aligned} \quad (2)$$

where x and $(1 - x)$ are the concentration of Ba^+ and Sr^+ ions, respectively. J_1, Ω_1 and μ_1 are the two-spin interaction ($J_{ij} = J$), the tunnelling frequency and dipolar moment of pure $BaTiO_3$, and J_2, Ω_2 and μ_2 are the corresponding parameters of pure $SrTiO_3$. The parameters of pure materials fit well with the experimental data.[20,21] They are listed in Table 1. We suppose four-spin interaction $J_{ijkl} = FJ_{ij} = FJ$, where F is the ratio of the four-spin coupling strength to the two-spin coupling strength, describing the ferroelectric distortion. Pure $BaTiO_3$ undergoes the first-order phase transition at the Curie point, which makes it necessary to consider the four-body interactions. $F = 2.6m^4/C^2$ as in Ref.[19]. Simultaneously, the x-ray absorption near-edge structure (XANES),[22] as a probe of the local atomic structure of the titanate perovskite, shows that the distortion of $SrTiO_3$ from the ideal perovskite structure is minuscule, which is proven by the small pre-edge feature. Thus the ferroelectric distortion in pure quantum paraelectric $SrTiO_3$ can be approximately neglected: that is, $F = 0$.

Table 1.

J_1	3.83×10^{-21}J	J_2	3.26×10^{-22}J
Ω_1	4.9×10^{-21}J	Ω_2	1.1×10^{-21}J
μ_1	3.48×10^{-20}nm	μ_2	2.41×10^{-20}nm

Furthermore, due to the translation symmetry only being presented in the x–y plane, all the average pseudo-spins vary with different layers in BST films. Under mean-field approximation, the average pseudo-spin in the ith layer can be expressed as

$$m_i = < S_i^z > = \frac{< H_i^z >}{2|H_i|}\tanh\frac{|H_i|}{2k_BT}, \qquad 1 \leq i \leq N, \quad (3)$$

where N is the total number of the layers and

$$< H_i^z > = \sum_j J_{ij}m_j + \sum_{jkl} J_{ijkl}m_jm_km_l + 2\mu E$$

$$= \begin{cases} J[(4m_1 + m_2) + Fm_1(4m_1^2 + 4m_2^2)] + 2\mu E & i = 1, \\ J[(4m_i + m_{i-1} + m_{i+1}) + Fm_i(4m_i^2 + 4m_{i-1}^2 + 4m_{i+1}^2)] + 2\mu E & 1 < i < N, \\ J[(4m_N + m_{N-1}) + Fm_N(4m_N^2 + 4m_{N-1}^2)] + 2\mu E & i = N, \end{cases} \quad (4)$$

$$|H_i| = \sqrt{\Omega^2 + (< H_i^z >)^2}. \quad (5)$$

The polarization of the ith layer is defined as

$$P_i = 2n\mu < S_i^z >, \tag{6}$$

where n is the number of the dipoles per volume.

Then, because of doping, apart from the thermo-average, the true polarization has to include the structure-average, $\langle P_i\rangle = 2n\langle\mu\langle S_i^z\rangle\rangle$. Meanwhile, it is known from x-ray diffraction that in the BST system the lattice parameter increases with increasing x practically by the linear Vegard law:[13,14] Δa=0.01x (nm). The lattice constant a_0 of pure $SrTiO_3$ is approximately 0.3905nm. So the density of the dipolar moment in the doped system can be expressed as

$$n = \frac{1}{(a_0 + \Delta a)^3}. \tag{7}$$

Therefore, after considering the lattice expansion from doping, the polarization can be expressed as

$$\langle P_i\rangle = 2n\int_{J,\Omega,\mu} \mu\langle S_i^z\rangle P(J)P(\Omega)P(\mu)\mathrm{d}J\mathrm{d}\Omega\mathrm{d}\mu. \tag{8}$$

By simple algebra, we get a set of self-consistent equations for $\langle P_i\rangle$ instead of $\langle S_i\rangle$ (see Eq.(3)):

$$\begin{aligned}\langle P_i\rangle =& x^3 g_i(J_1,\Omega_1,\mu_1,F)\\ &+ x^2(1-x)g_i(J_1,\Omega_1,\mu_2,F)\\ &+ x^2(1-x)g_i(J_1,\Omega_2,\mu_1,F)\\ &+ x(1-x)^2 g_i(J_1,\Omega_2,\mu_2,F)\\ &+ x^2(1-x)g_i(J_2,\Omega_1,\mu_1,0)\\ &+ x(1-x)^2 g_i(J_2,\Omega_1,\mu_2,0)\\ &+ x(1-x)^2 g_i(J_2,\Omega_2,\mu_1,0)\\ &+ (1-x)^3 g_i(J_2,\Omega_2,\mu_2,0),\end{aligned} \tag{9}$$

where we define the function

$$g_i(J,\Omega,\mu,F) = 2n\mu\frac{\langle\langle H_i^z\rangle\rangle}{2\parallel H_i\parallel}\tanh\frac{\parallel H_i\parallel}{2k_{\mathrm{B}}T}, \tag{10}$$

and

$$\begin{aligned}&\langle\langle H_i^z\rangle\rangle\\ &= \begin{cases} J\left[\frac{1}{(2n\mu)}(4\langle P_1\rangle + \langle P_2\rangle) + \frac{F}{(2n\mu)^3}\langle P_1\rangle(4\langle P_1\rangle^2 + 4\langle P_2\rangle^2)\right] + 2\mu E & i = 1,\\ J\left[\frac{1}{(2n\mu)}(4\langle P_i\rangle + \langle P_{i-1}\rangle + \langle P_{i+1}\rangle) + \frac{F}{(2n\mu)^3}\langle P_i\rangle(4\langle P_i\rangle^2 + 4\langle P_{i-1}\rangle^2 + 4\langle P_{i+1}\rangle^2)\right] + 2\mu E & 1 < i < N,\\ J\left[\frac{1}{(2n\mu)}(4\langle P_N\rangle + \langle P_{N-1}\rangle) + \frac{F}{(2n\mu)^3}\langle P_N\rangle(4\langle P_N\rangle^2 + 4\langle P_{N-1}\rangle^2)\right] + 2\mu E & i = N,\end{cases}\end{aligned} \tag{11}$$

$$\parallel H_i\parallel = \sqrt{\Omega^2 + (\langle\langle H_i^z\rangle\rangle)^2}. \tag{12}$$

Finally, the total average of polarization of BST film with N layers is $\langle P\rangle = \frac{1}{N}\sum_{i=1}^{N}\langle P_i\rangle$. Consequently, the average dielectric susceptibility of thin films is given by

$$\chi = \frac{1}{N}\frac{\sum_{i=1}^{N}\partial\langle P_i(E,T)\rangle}{\partial E}\bigg|_{E=0}. \tag{13}$$

By solving Eqs.(9)–(13), we can discuss the thermodynamic properties of BST films.

3. Numerical results and discussion

Our model reveals some features of $Ba_xSr_{1-x}TiO_3$ thin films. In our following discussion, N represents the layer number of thin films. The numerical calculation for dielectric susceptibility of $Ba_xSr_{1-x}TiO_3$ thin film shows that there exists a critical concentration x_c, which distinguish $SrTiO_3$-like and $BaTiO_3$-like behaviour for the doped system. For x below x_c, its susceptibility saturates at a high value at low temperature and its spontaneous polarization always remains zero even at 0K. This means that the system keeps the features of the quantum paraelectrics like pure $SrTiO_3$, which has been called the glasslike state.[8,11,13] This kind of behaviour might be understood in the following way. The too-little doping is not enough to suppress the large ground state quantum fluctuation arising from $SrTiO_3$, and ferroelectricity cannot been induced in this case. For x higher than x_c, doping can modify the low-temperature state dramatically and the round peak of susceptibility appears. At this time a polar state is induced by doping. The peak position shifts to high temperature with increasing x. Figure 1 shows the concentration depen-

dence of T_m, at which the dielectric susceptibility is the maximum. From Fig.1, we find that when Ba^{2+} concentration substituted into the structure of $SrTiO_3$ is greater than a certain critical value, the peak temperature of BST films increases with the increasing doping concentration. This result is in fairly good agreement with Ref.[15]. The relation $T_m \propto (x - x_c)^{\frac{1}{2}}$ when x is slightly higher than x_c is satisfied.[10,23]

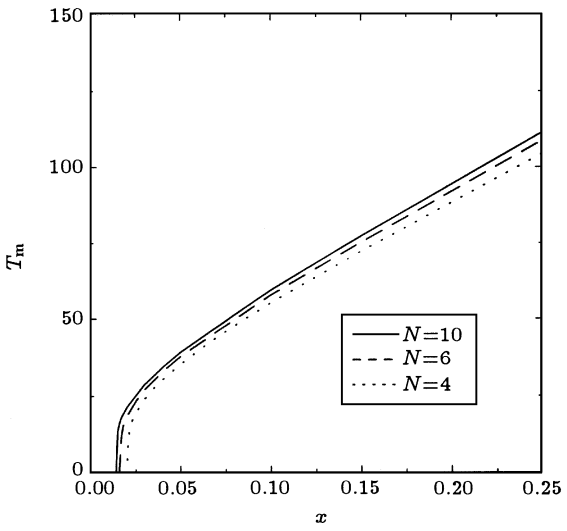


Fig.1. Peak temperature as a function of doping concentration.

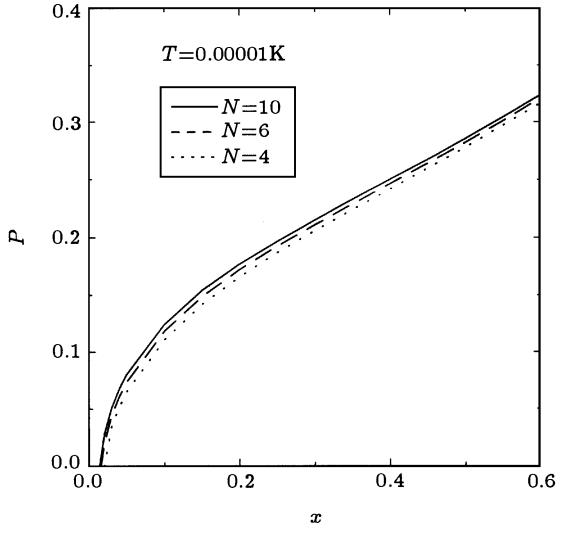


Fig.2. Concentration dependence of spontaneous polarization at T=10^{-5}K.

The mean spontaneous polarization depending on concentration at 10^{-5}K is presented in Fig.2. The result indicates that polarization appears at the critical concentration and monotonically increases with increasing concentration of barium, and the speed of increase in polarization slows down with the continuous increase of x. This behaviour agrees with experimental results for KTL [24,25] and KIN,[26] which are analogous to the BST system.[15]

The influence of film thickness on BST film is also observed from Figs.1 and 2. The peak temperature T_m and critical concentration x_c vary with the film thickness. Here the relation between peak temperature and Ba^{2+} concentration can be rewritten as $T_m = A(N)[x - x_c(N)]^{\frac{1}{2}}$. Figure 2 fits well with $\langle P \rangle = B(N)[x - x_c(N)]^{\frac{1}{2}}$. All the corresponding parameters are listed in Table 2.

Table 2.

N	x_c	$A(N)$	$B(N)$
10	0.014	219.7	0.410
6	0.016	215.7	0.405
4	0.02	208.4	0.400

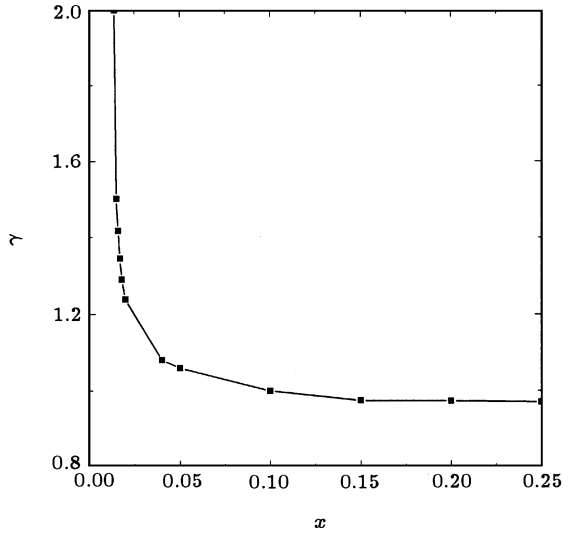


Fig.3. Critical exponent γ as a function of Ba^{2+} concentration.

On the other hand, the parabolic relation $T_m \propto (x - x_c)^{\frac{1}{2}}$ between T_m and x is a typical relation for a quantum ferroelectric behaviour. It is theoretically predicted [27,28] that the critical exponent γ, which is obtained by fitting χ on the high temperature side of T_m to the equation

$$\chi = C(T - T_m)^{-\gamma}, \tag{14}$$

should be 2 at $x = x_c$. γ is regarded as a proper parameter to describe quantum fluctuation behaviour, and show the deviation from the Curie–Weiss law. By fitting χ data, from our numerical calculation for N=10 BST thin film in the temperature range of

T_m+20K< T < T_m+50K to Eq.(14), γ is figured in Fig.3. For $x > 0.15$, γ has the classical value. With decreasing x, γ increases monotonically, indicating the increasing influence of the quantum effects.

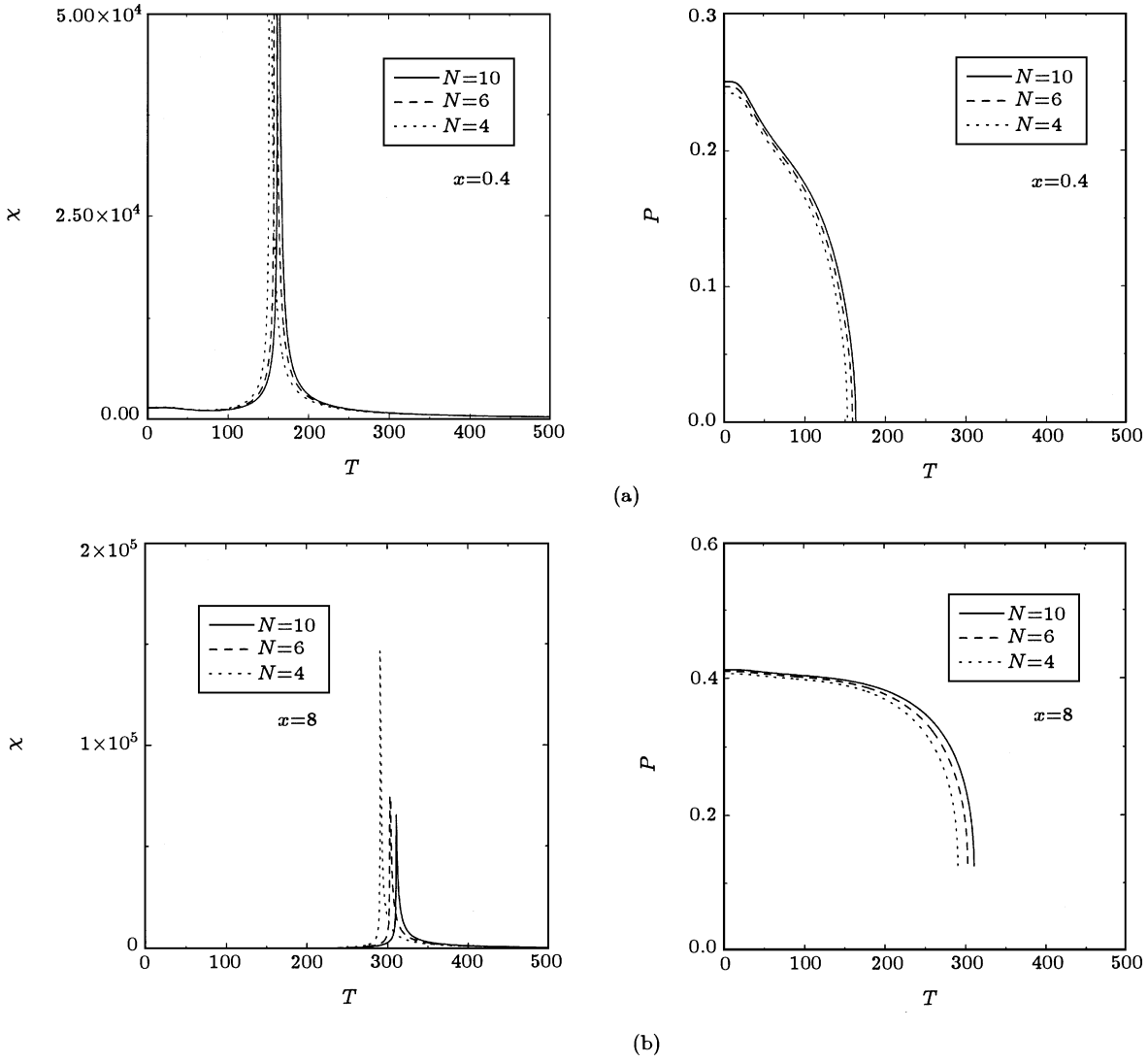


Fig.4. (a) Temperature dependence of mean spontaneous polarization and dielectric susceptibility at x=0.4. (b) Temperature dependence of mean spontaneous polarization and dielectric susceptibility at x=0.8.

As mentioned above, ferroelectric phase transition occurs for $x > x_c$. The temperature dependences of the dielectric susceptibility and spontaneous polarization of doped BST thin film are shown in Fig.4. Here we investigate their transition behaviours at different doping concentrations carefully. Both cases for x=0.4 and x=0.8 are given in Figs.4(a) and (b), respectively. Obviously, when x=0.4 the second-order phase transition occurs with the characteristics that spontaneous polarization continuously changes from nonzero to zero in the vicinity of T_m and the dielectric peak diverges at T_m. However, at $x = 0.8$ the first-order phase transition occurs where spontaneous polarization discontinuously changes from nonzero to zero and in the vicinity of T_m the dielectric peak converges. Meanwhile, T_m shifts to high temperature with increasing layer number in both cases. It can be concluded that for BST thin film there exists another critical concentration x_{c1}, which separates the first and second phase transition behaviour.

Figure 5 shows the relationship between the temperature and the average dielectric susceptibility at $x = 0.8$ when electric field is applied. Comparing with Fig.4, the existence of the electric field leads to the decrease of dielectric susceptibility in the whole temperature range. Such a tendency has already been

observed in many experiments and has been widely acknowledged. From Figs.4 and 5, we notice that the effect of the thickness of thin film on dielectric susceptibility is opposing in different temperature ranges. In the $T < T_{\rm m}$ range dielectric susceptibility enhances with the thickness of thin films and vice versa in the $T > T_{\rm m}$ range.

In order to further discuss the characteristics of phase transition in BST thin films, we calculate their hysteresis loops. As we all know, for $x < x_{\rm c}$ no hysteresis loops are observed. We show the hysteresis loops of BST thin film in Fig.6 in the range of $x > x_{\rm c}$. Here we still select two special concentrations of Ba^{2+} to discuss. In Fig.6(a) the typical ferroelectric hysteresis loops with second-phase characteristic are observed at x=0.4. In Fig.6(b) with x=0.8, the features of the first-order phase transition in which double hysteresis loops appear are found when the temperature is slightly higher than $T_{\rm m}$.

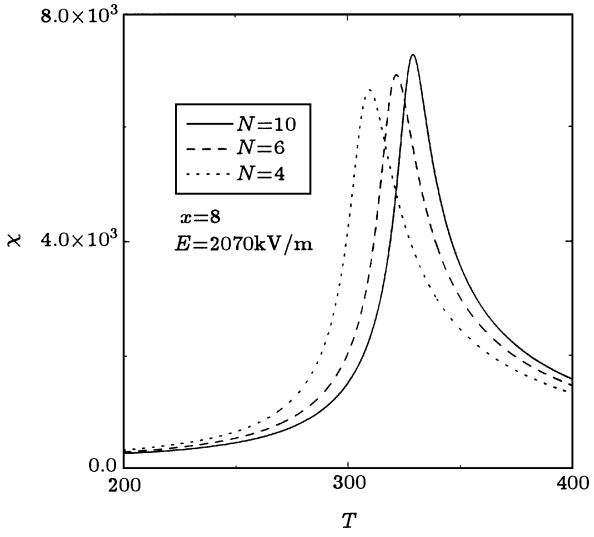


Fig.5. Temperature dependence of dielectric susceptibility at x=0.8 in applied electric field.

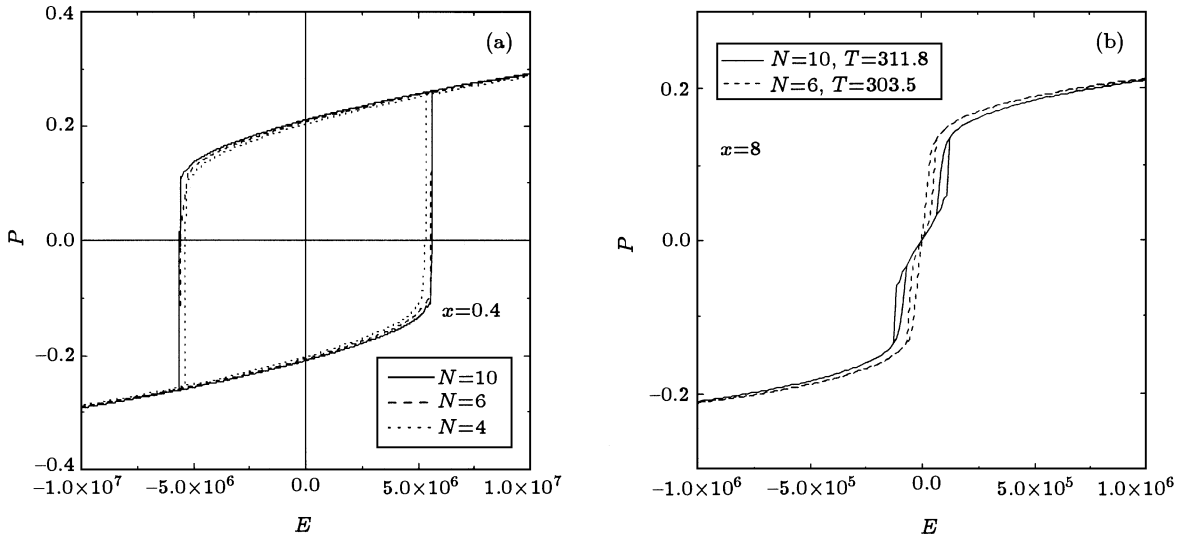


Fig.6. (a) Ferroelectric hysteresis at x=0.4 at T=60K. (b) Ferroelectric hysteresis at x=0.8 at different temperature.

In summary, we study the properties of $Ba_x Sr_{1-x}TiO_3$ thin films based on TIM within the framework of mean field theory. The double peak distribution model of related parameters is applied to simulate doping and the lattice expansion due to doping with large Ba^{2+} is taken into account. The quantum effects arising from doping are also investigated. We find that the dielectric and phase transition behaviours of BST thin film are strongly related to doping concentration. Our results are in good agreement with experiment.

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