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A study of the impurity-induced phase transition in $Ba_xSr_{1-x}TiO_3$ within the framework of the transverse-field Ising model

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Abstract

The transverse-field Ising model is successfully applied to the $Ba_xSr_{1-x}TiO_3$ system. An impurity-induced paraelectric–ferroelectric phase transition is found for proper parameters. An explanation is offered for the results of the susceptibility $\chi(x, T)$, the transition temperature $T_m(x)$, the spontaneous polarization $\langle P \rangle$ versus x and versus T, the field dependence of $\chi(x, T)$ and that of the polarization $\langle P \rangle$ versus E for x, $0.2 \leqslant x \leqslant 0.95$.

1. Introduction

Quantum paraelectrics constitutes a unique subject of great interest, in which polar long-range ordering is suppressed by sufficiently high quantum fluctuations [1]. This unusual feature has mainly been investigated in perovskite-like strontium titanate ($SrTiO_3$) and potassium tantalate ($KTaO_3$), in which remarkably high dielectric permittivity at low temperatures was found and no ferroelectric phase transition was detected [2]. To some extent quantum paraelectrics can be classified as marginal systems, which are at the limit of the stability of the paraelectric phase. Such stability can be destroyed by small perturbations from the external electric field and impurities. It has been found in $SrTiO_3$ that a small content of impurities such as Ba, Ca and Pb induces a ferroelectric phase transition with a transition temperature proportional to $(x - x_c)^{\frac{1}{2}}$ [2], where x is the impurity molar concentration and x_c is the critical concentration (quantum limit).

In $BaTiO_3$ the presence of polar clusters above the phase transition temperature is believed [3] to be linked with the cross-over from the displacive to the order–disorder limit, which is testified by the experimental observation of a strong polar relaxation mode in the frequency range 10^8–10^9 Hz [4]. Thus the order–disorder behaviour becomes important near its cubic–tetragonal phase transition point, and it is enlightening to use an order–disorder

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model to explain its ferroelectric phase transition. The transverse-field Ising model (TIM) has been proposed [5–7] to treat the interaction of the dipolar moments as well as the quantum mechanical effects within a unified framework. The TIM has also been extended to pure quantum paraelectrics [8], successfully deducing the Barret formula [9] that describes the temperature dependence of the dielectric susceptibility of pure quantum paraelectrics over the whole temperature range.

So in $Ba_xSr_{1-x}TiO_3$ (BST) it is rational for us to apply the TIM to obtain good estimate of this system directly from the information available on the pure materials $SrTiO_3$ and $BaTiO_3$ by averaging some key quantities. In the present work, the doped quantum paraelectric is studied within the framework of the TIM. In particular, the random bond model usually applied to the magnetic system is adopted to consider the impurity effect. Furthermore, the well fitted parameters of the pure materials from the experimental data are used despite some approximate treatment. The concentration dependence of some quantities that are related to the phase transition properties in BST is paid heed to and discussed in detail in the present paper. We find that the properties of both pure $BaTiO_3$ and $SrTiO_3$ are responsible for the phase transition in BST. The system retains the features of a quantum paraelectric as the Ba concentration is lower than the critical concentration x_c, but exhibits the features of a normal ferroelectric with increase in the Ba concentration. Furthermore, through our numerical calculation we believe that when the impurity concentration is slightly higher than x_c, the transition temperature is approximately proportional to $(x - x_c)^{\frac{1}{2}}$. At medium Ba concentrations, e.g. $x = 0.4$, 0.5 and 0.6, the system exhibits the typical features of a second-order ferroelectric phase transition, while for $x = 0.8$ the character of the first-order ferroelectric phase transition is detected, from which we conclude that there exists another critical concentration x_{c1} in the range of $x = 0.6$–0.8, where a crossover from the second-order phase transition to the first-order phase transition occurs.

It should be noted that similar numerical calculations have been carried out on the related system $Sr_{1-x}Ca_xTiO_3$ [5, 6, 10–12]. In order to explain anomalies occurring at $x > 0.1$ the lattice collapse due to the small Ca^{2+} ion was accounted for by piezoelectric coupling [13]. In the present study on BST, similar effects due to lattice expansion by doping with large Ba^{2+} ions are taken into account by corrections to the pseudospin density (see below).

2. Models and analysis

The BST system is considered within the framework of the TIM. The random bond model for a magnetic mixed system is applied simultaneously in the present paper to consider the impurity effect. The Hamiltonian is given by:

$$H = -\Omega \sum_i S_i^x - \tfrac{1}{2} \sum_{i,j} J_{ij} S_i^z S_j^z - 2\mu E \sum_i S_i^z, \tag{1}$$

where $i \neq j$, $S_i = \frac{1}{2}$ and $-\frac{1}{2}$ for up and down pseudospins, E represents the external electric field, μ is the effective dipolar moment of each spin, J_{ij} denotes the nearest-neighbour pseudospin interaction, the summation $\sum_j J_{ij} = J$ covers the nearest neighbours of site i, and Ω is the tunnelling frequency. Here we apply the double-peak distribution when considering the effect of the impurities. The distribution functions can be expressed as follows:

$$P(J) = x\delta(J - J_1) + (1 - x)\delta(J - J_2), \tag{2}$$

$$P(\Omega) = x\delta(\Omega - \Omega_1) + (1 - x)\delta(\Omega - \Omega_2), \tag{3}$$

$$P(\mu) = x\delta(\mu - \mu_1) + (1 - x)\delta(\mu - \mu_2), \tag{4}$$

where x and $1-x$ are the concentration of Ba and Sr ions respectively, J_1, Ω_1 and μ_1 are the pseudospin interactions, the tunnelling frequency and the effective dipolar moment of pure $BaTiO_3$, and J_2, Ω_2 and μ_2 are the corresponding parameters for pure $SrTiO_3$. In the limiting cases of $x = 0$ and 1 the TIM can well describe the property of pure $BaTiO_3$ and that of pure $SrTiO_3$. According to equation (1) one can obtain the dielectric susceptibility as well as the mean polarization of pure $BaTiO_3$ and $SrTiO_3$ under a mean-field approximation on a single ion [8, 14]. The fitting parameters of pure $BaTiO_3$ are given in [14]. Within the framework of a mean-field approximation we fit the experimental data and obtain J_2, Ω_2 and μ_2 of pure $SrTiO_3$ [15]. We show some of these parameters in table 1. For pure $BaTiO_3$ a very important aspect is that it undergoes a first-order phase transition at the Curie point, which makes it necessary to take into account the modification due to the ferroelectric distortion. So the nearest-neighbour pseudospin interaction constant in pure $BaTiO_3$ is assumed to be modified as follows:

$$J_1 = J_{10}(1 + F_2P^2 + F_4P^4 + F_6P^6), \tag{5}$$

where P is the polarization and $J_{10} = 2.3 \times 10^{-20}$ J is the original interaction constant when the ferroelectric distortion is not considered. $F_2 = 2.6m^4/C^2$, $F_4 = 2.6m^8/C^4$ and $F_6 = -860m^{12}/C^6$ describe the contribution of the ferroelectric distortion [14]. According to equation (5) we find that modification of the interaction constant leads to the same results as the addition of the four-body, six-body and eight-body interactions under the mean-field approximation on a single ion, which explains the experimental results more appropriately and accurately [14, 16].

On the other hand the x-ray absorption near-edge structure (XANES) [17] 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 and the interaction constant J_2 in pure $SrTiO_3$ is a constant as $J_2 = 1.96 \times 10^{-21}$ J. To reduce the number of adjustable parameters we assume μ_1, Ω_1, μ_2 and Ω_2 as four constants in the following calculations.

According to the TIM, under the mean-field approximation on a single ion the polarization $\langle P\rangle = 2N\langle\mu\langle S^z\rangle\rangle$, where N is the density of the dipolar moment, $\langle S^z\rangle$ is the thermo-average of the pseudospin and $2N\langle\mu\langle S^z\rangle\rangle$ denotes the total average of the polarization when the thermo-average as well as the composition average is taken into account. Actually the density of the dipolar moment in BST varies with different Ba contents because the lattice parameter in this system approximately varies with the impurity concentration via a linear Vegard law: $\Delta a = 0.1x$, where Δa is the increment of the $SrTiO_3$ lattice constant in a sample with Ba concentration x and the lattice parameter a_0 in pure $SrTiO_3$ is approximately 3.905 Å. In dealing with the Hamiltonian above we apply the mean-field approximation on a single ion. So several important physical quantities related to the phase transition properties in the mixed system are expressed as follows:

$$N = \frac{1}{(a_0 + \Delta a)^3}, \tag{6}$$

$$\langle P\rangle = 2N\langle\mu\langle S^z\rangle\rangle = 2N\int_{J,\Omega,\mu}\mu\langle S^z\rangle P(J)P(\Omega)P(\mu)\,\mathrm{d}J\,\mathrm{d}\Omega\,\mathrm{d}\mu \tag{7}$$

$$\langle S^z\rangle = \frac{\mathrm{Tr}\,S^z\exp(-\beta H)}{\mathrm{Tr}\exp(-\beta H)}, \tag{8}$$

$$\chi = \frac{1}{\varepsilon_0}\frac{\mathrm{d}\langle P\rangle}{\mathrm{d}E} \tag{9}$$

where χ is the dielectric susceptibility.

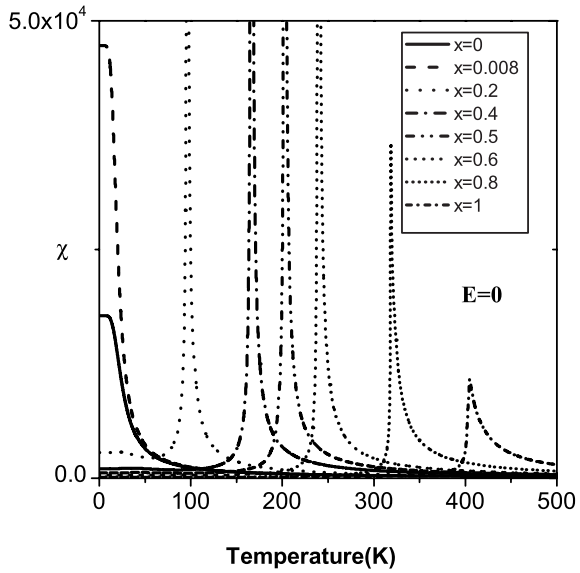

Figure 1. The temperature dependence of the dielectric susceptibility at different concentrations in the absence of an electric field.

Table 1. Fitting parameters of pure $BaTiO_3$ (1) and pure $SrTiO_3$ (2).

Ω_1	μ_1	Ω_2	μ_2
4.9×10^{-21} J	2.17 e Å	1.1×10^{-21} J	1.51 e Å

3. Results and discussion

Our model qualitatively reveals many basic features of doped quantum paraelectrics in spite of the remaining small deviations. The temperature dependence of the dielectric susceptibility of doped quantum paraelectrics for various impurity concentrations (figure 1) approaches that of the experimental data [18]. In the case of $x = 0.008$, the low-T susceptibility is strongly enhanced in contrast to the $x = 0$ case, although a similarity between them is exhibited. To the best of our knowledge it is the quantum fluctuation that stabilizes the paraelectric phase and causes the deviation of the dielectric susceptibility from the Curie–Weiss law and its saturation at low temperatures. When a very small concentration of impurities is mixed with pure $SrTiO_3$, the deviation from the Curie–Weiss law is reduced and the saturation reaches a much higher value because of the weakened quantum effect. According to figure 1 we are sure that the critical concentration x_c, where a peak begins to appear on the dielectric susceptibility, must be observed. When $x > x_c$, the quantum fluctuation in this system is too weak to stabilize the paraelectric state and the ferroelectric state inevitably appears. The temperature at which the dielectric susceptibility maximizes shifts to higher temperatures with increase in the impurity content. For $x = 0.8$ and 1.0 we may find that there is an evident decrease of the dielectric maximum, which indicates the occurrence of the first-order ferroelectric phase transition. So we conclude that another critical concentration x_{c1}, at which the ferroelectric phase transition varies from second- to first-order, is to be detected within the concentration range $x = 0.6$–0.8. Obviously both the pure quantum paraelectric and the impurities are responsible for the occurrence of the impurity-induced phase transition.

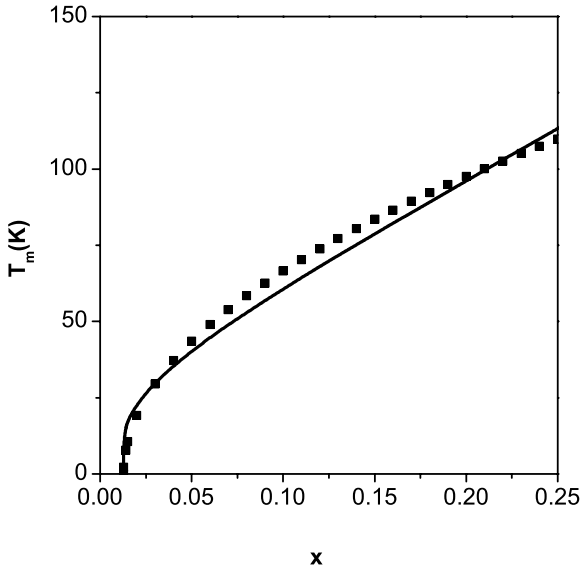

Figure 2. The concentration dependence of T_m. The solid curve is our theoretical result and the symbols depict $T_m \propto (x - x_c)^{\frac{1}{2}}$.

The concentration dependence of T_m, at which the dielectric susceptibility maximizes, is presented in figure 2. It is clear that there exists a critical concentration $x_c = 0.013$, below which T_m remains 0 K and the system retains the features of a quantum paraelectric. Other studies [2, 19] figured out that T_m versus x approximately follows the relation $T_m \propto (x - x_c)^{\frac{1}{2}}$ when x is small. According to figure 2 the solid curve is our results and the symbols depict $T_m \propto (x - x_c)^{\frac{1}{2}}$. They are in fairly good agreement.

The mean spontaneous polarization versus x at $T \rightarrow 0$ is shown in figure 3. The polarization appears at the critical concentration and increases quickly when x is very small. But with the continuous increase of x the increase in the spontaneous polarization slows down. Such a tendency is in good agreement with the experimental data obtained close to 0 K for $Li_xK_{1-x}TiO_3$ [20, 21], which is very similar to the BST system.

To obtain a clear picture of the phase transition in BST we plot the temperature dependence of the mean polarization for various Ba concentrations (figure 4). Although the evident second-order phase transition can be observed for $x = 0.2$, 0.4 and 0.6, the first-order phase transition tends to occur for higher Ba concentrations. In the case of $x = 0.8$ the typical features of a first-order ferroelectric phase transition are clearly seen, indicating the existence of another critical concentration x_{c1}.

In the rest of the paper we discuss the effect of the external electric field on BST. Figure 5 shows the temperature dependence of the dielectric susceptibility for $x = 0.008$ for different electric fields. It is obvious that with an increase in the electric field the dielectric susceptibility exhibits a remarkable decrease, especially at very low temperatures. Most interestingly, although the low-T dielectric susceptibility is temperature independent under a low electric field, a round peak is observed under a higher electric field. And it slightly shifts towards higher temperatures with increase in the electric field. Such behaviour is very similar to that in pure $SrTiO_3$ [7]. For both systems one can explain the appearance of the round peak as the onset of the electric field-induced ferroelectric order, although this interpretation is not accepted unanimously [11].

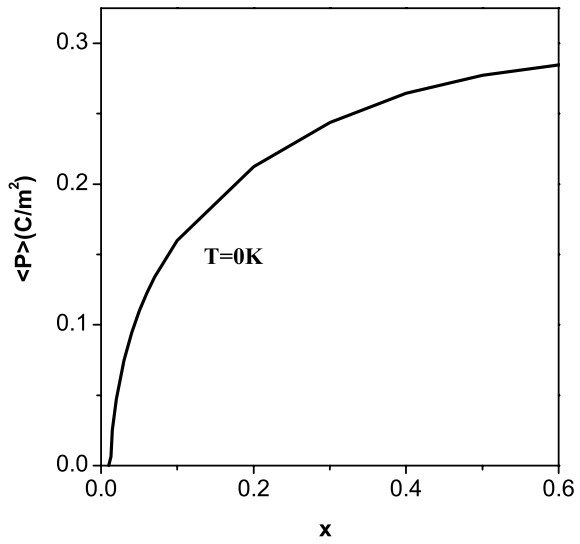

Fig.3

Figure 3. The concentration dependence of the mean spontaneous polarization at temperatures close to 0 K.

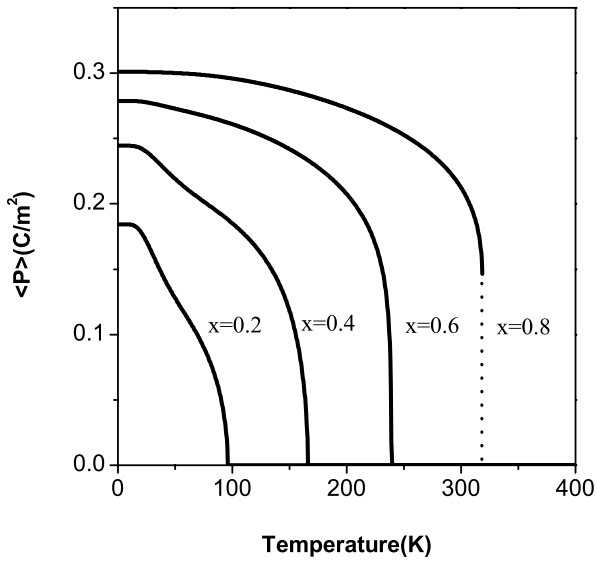

Figure 4. The temperature dependence of the mean polarization at different impurity concentrations.

Figure 6 shows the temperature dependence of the dielectric susceptibility for medium impurity concentrations of $x = 0.4$, 0.5 and 0.6 when various electric fields are applied. The similarity among them is that with increase of the electric field the dielectric susceptibility decreases over the whole temperature range. Such a variational tendency is more evident in the vicinity of T_m. Furthermore T_m shifts to higher temperatures with increase of the electric field. All these similarities bear the common characteristics of a second-order ferroelectric

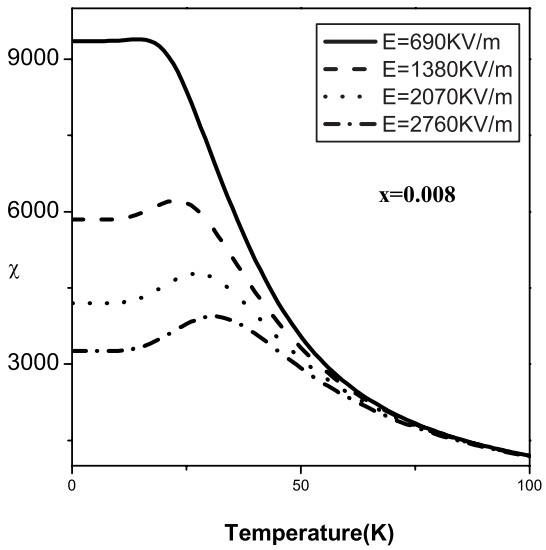

Figure 5. The temperature dependence of the dielectric susceptibility for the concentration $x = 0.008$ under different electric fields.

phase transition. It is found that with increase in the impurity concentration the maximum of the dielectric susceptibility reaches a higher value under the same electric field. At the same time the electric field has a greater effect on the dielectric susceptibility as well as on T_m with increase in the Ba concentration.

In figure 7 one can find several interesting characteristics of dielectric susceptibility for $x = 0.8$, which differs from the characteristics shown in figure 6. The dielectric susceptibility decreases with increase in the electric field below T_m, which is similar to the property shown in figure 6. Within a temperature range slightly higher than T_m, however, the dielectric susceptibility exhibits a small increase with increase in the electric field. The common characteristics for $x = 0.8$ under various electric fields is that T_m becomes higher with enhancement of the electric field. This indicates a first-order phase transition and is similar to the behaviour found for pure $BaTiO_3$.

Figure 8 shows the ferroelectric hysteresis for the mixed system with different Ba concentrations at 60 K ($x > x_c$), which is lower than the phase transition temperature even in the case of the lowest impurity content. Earlier experiments [19] measuring the hysteresis discovered similar features to ours. The lower the impurity content the narrower the ferroelectric hysteresis is. For $x < x_c$ the hysteresis will not be seen even at the much lower temperatures, which also conforms to the experimental results.

The ferroelectric hysteresis for a high impurity content is shown in figure 9. The designated temperature is slightly higher than T_m corresponding to the respective Ba concentration. An apparent double hysteresis is detected, which embodies the typical character of the field-induced phase transition and indicates exhibition of a first-order phase transition. With the increase in Ba concentration the double hysteresis becomes wider and shifts symmetrically to a higher external electric field and a lower one. When the impurity concentration decreases to $x = 0.6$ the double hysteresis cannot be seen and only the single hysteresis can be found at low temperatures.

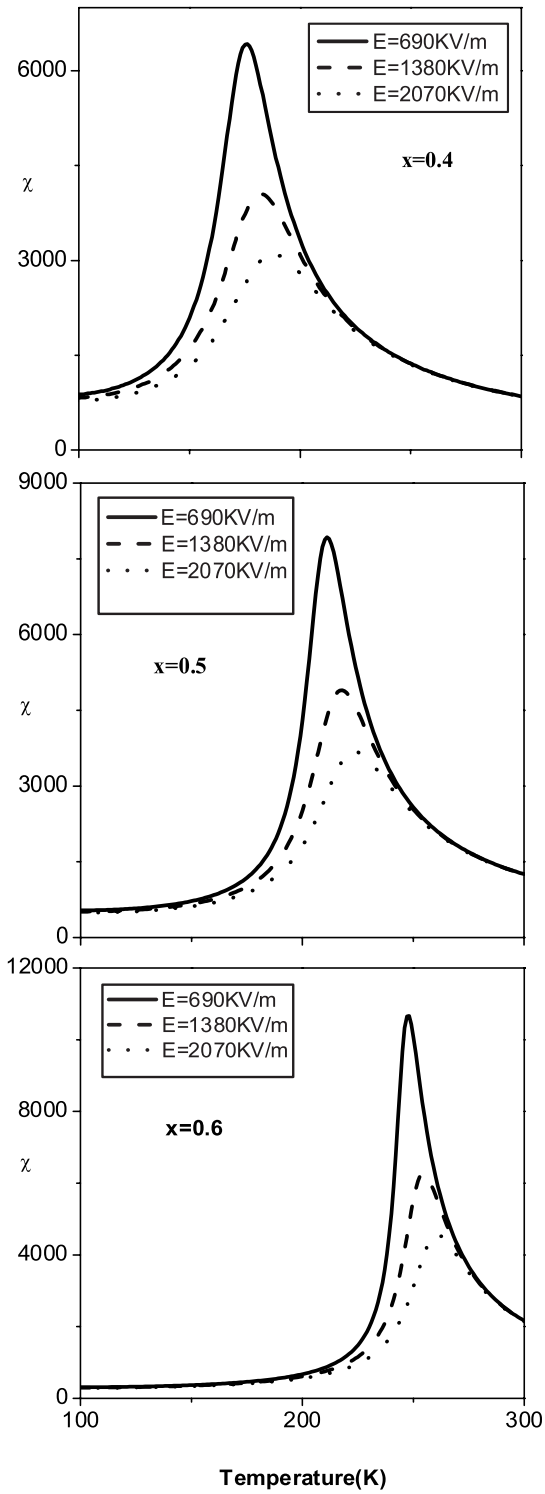

Figure 6. The dielectric susceptibility versus temperature under different electric fields for concentrations $x = 0.4$, 0.5 and 0.6.

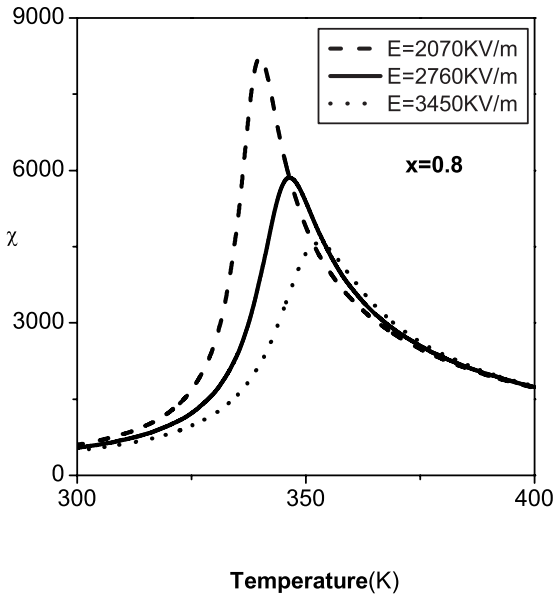

Figure 7. The temperature dependence of the dielectric susceptibility on the concentration $x = 0.8$ for different electric fields.

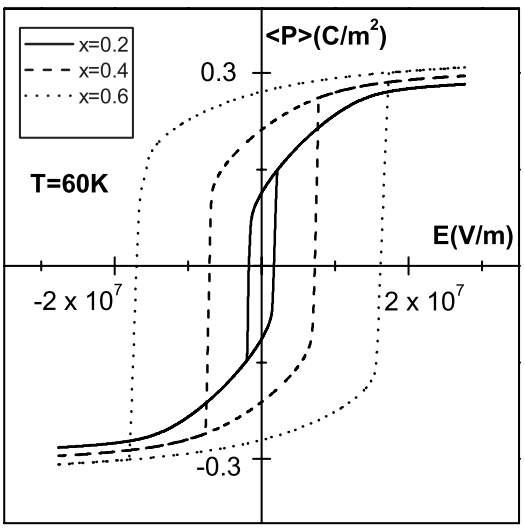

Figure 8. The dependence of the ferroelectric hysteresis on the impurity concentration at 60 K.

4. Summary

In the present work the TIM is applied to study the phase transition in BST. The random bond model usually used in the magnetic system is adopted for the consideration of the impurity effect. We find that both the materials are responsible for the properties of the phase transition in this system. When $x < x_c$, the dielectric behaviour as well as some other properties show features similar to pure $SrTiO_3$. With the increase in x the typical features of ferroelectrics

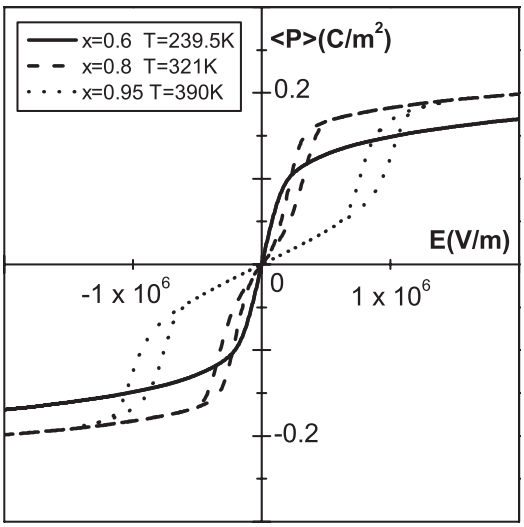

Figure 9. The double hysteresis for high impurity concentrations $x = 0.8$ and 0.95 at temperatures slightly higher than T_m.

tend to be found. When x is slightly higher than the critical concentration x_c, T_m shows a concentration dependence as $T_m \propto (x - x_c)^{\frac{1}{2}}$. For medium concentrations $x = 0.4$, 0.5 and 0.6, the whole system exhibits the typical characteristics of a second-order phase transition, which can also be seen from the results under the different electric fields. When x increases to a high concentration, the impurities have the predominant effect on the BST system and the typical features of a first-order phase transition are detected.

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