

Phase diagram and piezoelectric response of $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ solid solution

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Abstract. We report the phase diagram of $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ solid solution. It is found that substitution of smaller Ca ions for Ba ions can slightly increase the cubic-tetragonal (T) para-ferroelectric phase transition temperature and strongly decrease the T -orthorhombic (O) and O -rhombohedral (R) transition. This unique ferroelectric phase evolution is attributed to Ca off-centering effects. More importantly, lowering of the $T - O$ or $O - R$ phase transitions allows us to prepare the piezoelectric ceramics with a strain response as high as $S/E \approx 800$ pm/V ($E=10$ kV/cm) over a wide range of compositions with $x \approx 0.1 - 0.18$ at room temperature, which may be interesting for piezoelectric applications.

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BaTiO₃(BTO) was the first commercial piezoelectric ceramic [1], and it is being used in industry, for example, in sonar transducers used in fishfinders.[2] Its large piezoelectric response is essentially due to large lattice distortion under an electric field [3] and the easy switching of ferroelectric domains facilitated by a low coercive field.[4] Due to these large piezoelectric effects, BTO is also commonly used to develop new lead-free piezoelectric materials.[5, 6]

The ferroelectricity of BTO with an ABO₃ perovskite structure originates from the Ti-shift in the BO₆ octahedron, giving rise to three ferroelectric phases in the crystal: the tetragonal(*T*) phase with spontaneous polarization $P_s \parallel [001]_c$, orthorhombic(*O*) phase with $P_s \parallel [011]_c$ and rhombohedral(*R*) phase with $P_s \parallel [111]_c$. [7] Either A- or B-site substitution can change the state of spontaneous polarization, providing a variety of modifying phase evolutions and thus modifying the physical properties of BTO.[1] Among the various substitutions in the BTO system, Zr-substitution for B-site ions [8, 9, 10, 11] and Ca-substitution for A-site ions [6, 12, 13, 14, 15] are of particular interest.

When substituting Zr for Ti in BTO, one can observe an abundance of phase evolutions spanning from ferroelectric phases to relaxor or polar cluster states.[16] Even in the region of ferroelectric phases for Zr-substitution amounts of less than ≈ 20 mol%, ferroelectric phase evolutions are very complicated. In contrast to the monotonic decrease in the cubic (*C*)-*T* phase transition, the *T*-*O* and *O*-*R* phase transitions initially increase, reach a maximum at approximately 10 mol% substitution, and then decrease with increasing the Zr-substitution amount.[8, 17] Around the composition corresponding to the maximum transition point, the *T* – *O* and *O* – *R* phase transitions approach the *C* – *T* para-ferroelectric transition point. More interestingly, this solid solution shows a very large piezoelectric response,[10, 11] which has attracted much attention in the development of piezoelectric materials.[18, 19]

When substituting smaller Ca ions for bulky Ba ions, unique phase evolution[12, 13] and interesting physical phenomena [13, 14, 15] have been observed. In contrast to the reduction of the *C* – *T* para-ferroelectric transition for Zr substitution,[8, 17] this phase transition remains nearly unchanged for Ca-substitution in the limit of solid solution.[12, 13] However, the *T* – *O* and *O* – *R* transitions are shifted to lower temperatures such that $T^i \propto (x^i - x)^{1/2}$, where *i* denotes the phase boundaries of the *T* – *O* and *O* – *R* transitions, *x* is the Ca-substitution amount, $x^{O-R} = 0.180$, and $x^{T-O} = 0.233$. Although substitution of Ca for Ba results in the reduction of unit cell volume, which is naturally assumed to suppress the stability of the ferroelectric phase, the *C* – *T* transition remains nearly unchanged.[12, 13] This result suggests that a polarization component other than Ti displacement exists in $(\text{Ba}_{1-x}\text{Ca}_x)\text{TiO}_3$ crystal to compensate for pressure-induced ferroelectric instability and stabilize the ferroelectric *T* phase. This assumption is strongly supported by a first-principles calculation,[13] which predicts a Ca off-centering shift of 0.1 Å that is larger than the Ti shift in pure BaTiO₃ (0.05 Å).[17] This off-center displacement by smaller ions thus provides us an approach to control the ferroelectricity of perovskite oxide. Here, we examine the effects of Ca off-

centering on the phase evolution and piezoelectric response in $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ (BCZT) solid solution.

BCZT ceramics were prepared by a solid-state reaction approach. Mixtures of BaCO_3 , CaCO_3 , ZrO_2 and TiO_2 were calcined at 1823 K for 3 h. The calcined powders were ground, pressed and sintered at 1823 K for 5 h. The ceramic pellets were then electroplated with silver for electrical measurements. X-ray powder diffraction patterns were obtained using a Bruker AXS D8 ADVANCE diffractometer. The permittivities were measured using a Hewlett-Packard Precision LCR meter (HP4284A) at an ac level of 1V/mm. A cryogenic temperature system (Niki Glass LTS-250-TL-4W) was used to control the temperature within the range of 4 - 450 K. The electric-field-induced strain and dielectric hysteresis loops were measured using a ferroelectric measurement system (Toyo Corporation FCE-3) equipped with an Iwatsu ST-3541 capacitive displacement meter having a linearity of 0.1 % and a resolution of 0.3 nm.

Figure 1 shows X-ray diffraction patterns of BCZT solid solutions obtained at room temperature, from which we can observe the structure changing with composition. Very weak diffractions, which can be indexed by the orthorhombic structure of CaTiO_3 , were found in the compound with $x = 0.20$. This suggests that the limit of solid solution is less than 20 mol% in this system. Within the limit of solid solution, X-ray diffraction clearly indicated that there were structural changes in BCZT from R phase to O phase and then to T phase with increasing Zr-substitution amounts. X-ray diffraction patterns were well indexed as rhombohedral symmetry for samples with $x \leq 0.7$, as orthorhombic symmetry for sample with $x = 0.11$, and as tetragonal symmetry for samples with $x \geq 0.13$. The reflections in the 2θ range of 60 degree to 120 degree were then used to calculate the unit cell parameters by the method of least squares. The standard deviations of unit cell parameters were less than 0.0008 Å for all calculations. As shown by the variation of the lattice constant, due to the small ionic radius of Ca ions relative to Ba ions, substitution of Ca for Ba leads to a decrease in unit cell volume. It was found that the ferroelectric lattice distortion was very small in the BCZT solid solution. The distortion angles α in the R phase and β of the monoclinic unit cell in the O phase had only 0.01° and 0.1° deviations from the right angle, respectively, while the tetragonality c/a has a value of 1.005 for $x \geq 0.15$ in the T phase.

To observe the phase evolution with temperature, we measured the temperature variation of the permittivity. The results are shown in Fig. 2. For a composition of $x = 0$, the para-ferroelectric phase transition occurred at 363 K. Since the $T - O$ and $O - R$ phase transitions are very close to the $C - T$ transition, the transition temperatures are not easy to determine directly from the permittivity curve. However, these two transitions can be clearly determined from the differential curve, as shown in the inset of Fig.2. Here, we use the maximum point of the differential curve to define the $T - O$ and $O - R$ phase transitions; this contrasts with the case of the $C - T$ transition, which can be determined directly from the maximum of the permittivity curve. Using this approach, we established the phase diagram for this system, which is shown in Fig. 3. Similarly to the case of $(\text{Ba}_{1-x}\text{Ca}_x)\text{TiO}_3$, [12, 13] the $C - T$ para-

ferroelectric phase transition does not decrease with the reduction in unit cell volume associated with an increase in the Ca-substitution amount. A slight difference compared with $(\text{Ba}_{1-x}\text{Ca}_x)\text{TiO}_3$ is that the $C - T$ transition in BCZT initially increases from 363 K for $x = 0$ to 376 K for $x = 0.1$, after which it seems to reach saturation with further substitution. The change in the $T - O$ and $O - R$ phase transitions in BCZT is also very similar to that in $(\text{Ba}_{1-x}\text{Ca}_x)\text{TiO}_3$. [12, 13] Both the $T - O$ and $O - R$ phase transitions decrease with Ca-substitution. The similarity of the ferroelectric phase evolution in BCZT with that in $(\text{Ba}_{1-x}\text{Ca}_x)\text{TiO}_3$ strongly suggests that Ca off-centering effects play a critical role in tuning the polarization states in these two systems. [13]

We also examined the ferroelectric and piezoelectric behaviors in this system and show the results in Fig. 4. The remanent polarization P_r has an approximate value of $10 \mu\text{C}/\text{cm}^2$ and seems to remain unchanged within the limit of solid solution (Fig.3(b)), which is very similar to what is observed in $(\text{Ba}_{1-x}\text{Ca}_x)\text{TiO}_3$. [14] The coercive field of a BCZT ceramic usually falls in the range of 3 - 5 kV/cm. This low coercive field is favorable for electrical poling in a ceramic sample.

More interestingly, BCZT ceramics are extremely soft elastically. A surprisingly high elastic deformation of $\approx 0.15\%$ was observed in the ceramic under the application of a bipolar electric field of 20 kV/cm. This large electromechanical coupling was further confirmed by the strain response in a unipolar field. From the results of unipolar field measurements, it is clear that a strain level higher than that of commercial PZT ceramic is present in BCZT ceramics at the same electric field. To understand the large strain response in BCZT ceramics, we analyzed the variation of the effective piezoelectric constants defined by S/E (=the ratio of maximum strain to the applied electric field) and compared this variation with the phase evolution in the phase diagram. From Fig. 3(b), it is immediately clear that at a measurement temperature of $T=295$ K, BCZT solid solutions undergo phase changes between $R - O$ or $O - T$ states over compositions ranging from $x \approx 0.1$ to $x \approx 0.18$. This phase evolution is accompanied by the appearance of large effective piezoelectric constants for BCZT. Values of S/E greater than 800 pm/V were observed in this wide composition region. It is reasonable to consider that structural transformation plays a critical role in the large piezoelectric response in these solid solutions. As observed in the X-ray diffraction measurements, the ferroelectric distortions among the T , O and R ferroelectric phase are very small. Moreover, the difference in transition temperature between $R - O$ and $O - T$ transitions is approximately 20 K, indicating that the energy difference between these ferroelectric phases is very small. The small ferroelectric distortion together with the small energy difference between these ferroelectric phases are thought to facilitate the phase transformations, resulting in the large strain response under the application of an electric field in these solid solutions.

We further measured the dependence of strain response on the temperature for ceramic sample with $x = 0.1$ having large piezoelectric effects around room temperature in the temperature range of 228 K - 373 K. The results are summarized in Fig.4(d) and Fig.3(c). In this composition, the $R - O$ and $O - T$ phase boundaries cover the

temperature range of 290 K - 320 K. Just within this temperature range, the ceramic sample shows very large elastic deformation under the application of electric field. As temperature departs from this temperature range, the strain level also decreases. This again suggests that the $R - O$ and $O - T$ phase boundaries are responsible for the large electromechanical coupling effects in BCZT solid solutions. An interesting phenomenon for this material is that the strain response is very stable in the temperature range mentioned above, which might be of significance for the practical applications.

Here, it should be mentioned a recent report by Liu and Ren [18] on system of $(1 - y)\text{Ba}(\text{Ti}_{0.8}\text{Zr}_{0.2})\text{O}_3 - y\text{Ba}_{0.7}\text{Ca}_{0.3}\text{TiO}_3$, which shows a high piezoelectric coefficient of $d_{33} = 620$ pC/N at $y = 0.5$, triggering a great interest in this composition in the last two years. Liu and Ren state that the high piezoelectricity of composition is due to a morphotropic phase boundary (MPB) between a ferroelectric R and a ferroelectric T phases, which leads to a nearly vanishing polarization anisotropy and thus facilitates polarization rotation between $[001]_c T$ and $[111]_c R$ states. Actually, this composition is exactly the same as that demonstrated in the present system of $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ with $x = 0.15$. In contrast to Liu and Ren's statement, our phase diagram does not support the presence of a direct phase transition between R and T phase in this composition. Instead, our results indicate that this composition has the successive phase transitions of $C - T - O - R$ as BTO. This conclusion is also supported by the pyroelectric current measurements reported by Benabdallah *et al.*[20], in which three sharp peaks of pyroelectric currents corresponding to three phase transitions are demonstrated. Actually, when carefully examining the temperature dependence of permittivity of Liu and Ren's sample with $y = 0.5$, one can find that in addition to the $T - C$ transition and the so-called " $R - T$ " transition at T_{R-T} there is another phase transition at lower temperature.[18, 19] Therefore, we consider that the polymorphic phase transitions observed in our study can offer a reasonable explanation for the large piezoelectric response in the solid solution of $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ with $x = 0.15$. Actually, our samples with $x = 0.1 - 0.18$ having $R - O$ or $O - T$ phase transformations around room temperature all show very large piezoelectric response comparable to that with $x = 0.15$.

In summary, we have obtained the phase diagram of $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ solid solution. It was demonstrated that Ca off-centering plays a critical role in stabilizing the ferroelectric phase and tuning the polarization state in the $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ system. The Ca off-centering effect also allowed us to shift the $R - O$ and $O - T$ phase boundaries to room temperature, leading to the occurrence of electromechanical coupling effects, comparable to those of PZT, in the system over a large composition range.

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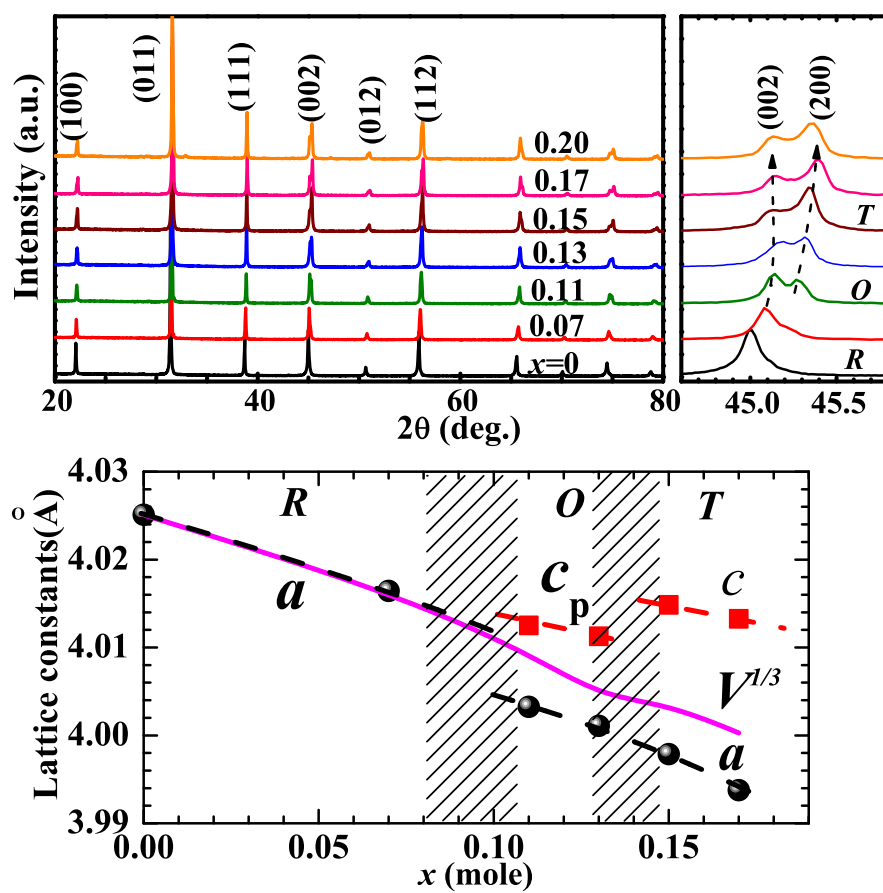


Figure 1. X-ray diffraction patterns and unit cell parameters of BCZT solid solutions obtained at room temperature.

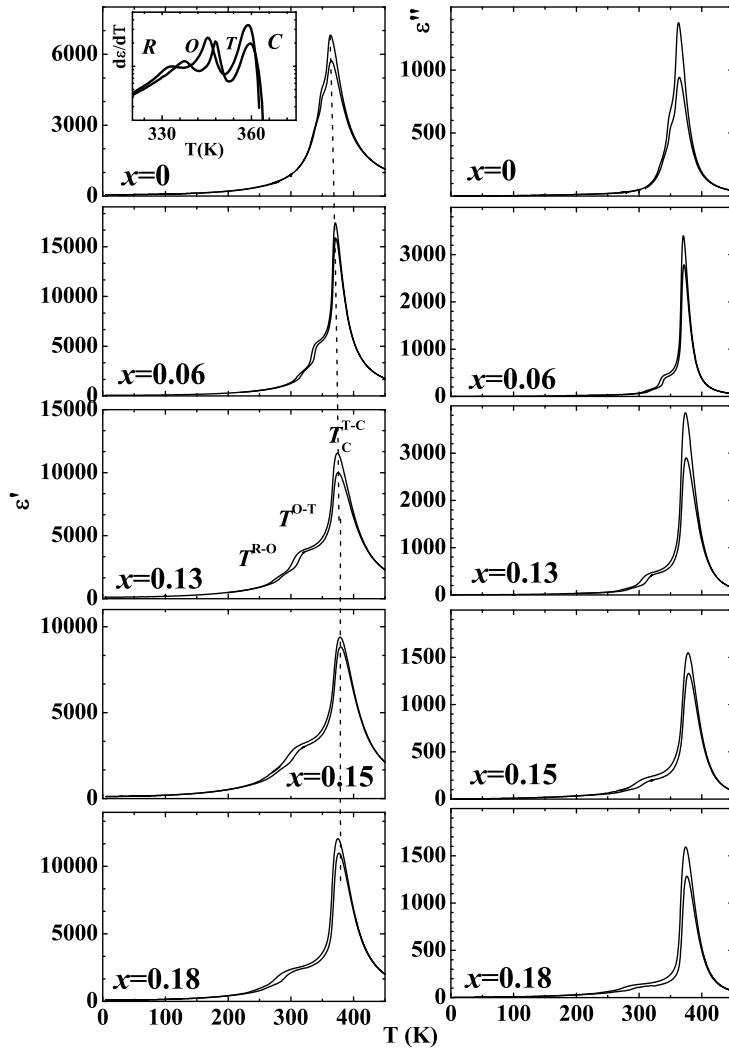


Figure 2. Temperature variation of the real (ϵ') and imaginary (ϵ'') parts of permittivity in BCZT solid solutions. Data were obtained at 100 kHz and an ac level of 1 V/mm.

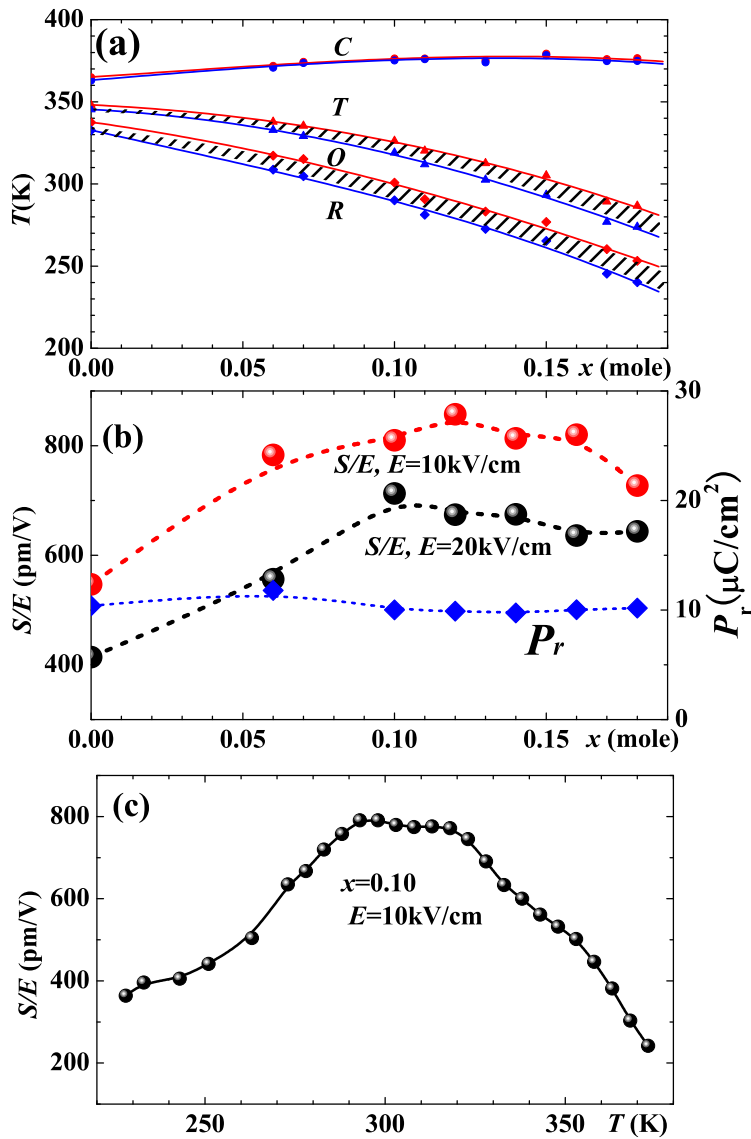


Figure 3. (a) Phase diagram of BCZT. The slanted line region indicates the thermal hysteresis of the phase transition. Thermal hysteresis of the $C - T$ transition is very small and is less than 2 K. (b) Variation of remanent polarization P_r and strain level S at $E=10$ and 20 kV/cm with composition at $T=295$ K. (c) Temperature dependence of strain level obtained at $E=10$ kV/cm for $x = 0.1$.

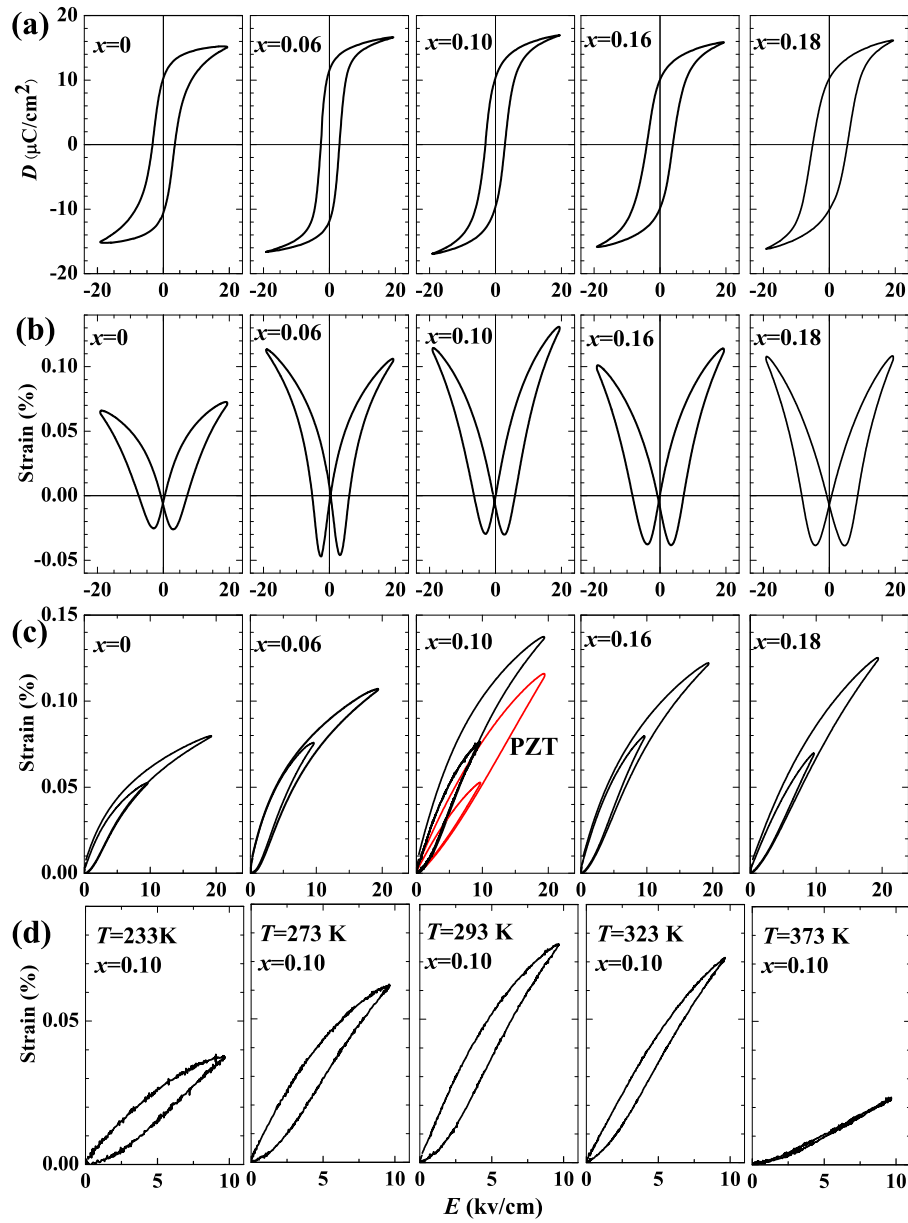


Figure 4. D – E hysteresis loop (a), and strain induced by the bipolar (b) and unipolar (c) electric fields in the BCZT piezoelectric ceramics at $T=295$ K. For comparison, the strain response of PZT ceramic in an unipolar field is also shown. (d) shows the temperature dependence of strain induced by the unipolar electric field $E=10$ kV/cm for $x = 0.1$.