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Large recoverable electrostrain in Mn-doped (Ba,Sr) TiO_3 ceramics

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In this letter we demonstrate that with a different principle, $BaTiO_3$ ceramics, so far considered as inferior piezoelectrics compared with $Pb(Zr,Ti)O_3$ (PZT), can show a large recoverable electrostrain. This principle utilizes a point-defect-mediated reversible domain switching mechanism, which can in theory generate 0.368% strain for $BaTiO_3$ ceramics at the best condition. Experimental results showed that, after aging at room temperature, 1.0 mol % Mn-doped $(Ba_{0.95}Sr_{0.05})TiO_3$ ceramics generate a large recoverable nonlinear strain of about 0.12%–0.15% at a field of 3 kV/mm. This value exceeds that of conventional hard PZT piezoelectric ceramics. A microscopic model for the domain-related electrostrain effect in ceramics is proposed. It is also found that the large electrostrain effect is quite stable with respect to both changing frequency and fatigue cycles. Large electrostrain remains recoverable down to 0.05 Hz and after 10 000 cycles. These results demonstrate the potential of our approach in achieving large recoverable electrostrain in environmental-friendly (Pb-free) ceramics. © *2004 American Institute of Physics*.

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Historically, $BaTiO_3$ was the first polycrystalline piezoelectrics (in the early 1950's),[1] but soon replaced by $Pb(Zr,Ti)O_3$ (PZT) ceramics because the latter has much better piezoelectric properties.[1] Since then, PZT has dominated piezoelectric applications to date. However, PZT is now facing a big challenge due to the environmental hazard by its toxic lead.[2,3]

Very recently, based on a different mechanism we found that a large electrostrain of 0.75% at 200 V/mm can be obtained in aged $BaTiO_3$-based ferroelectric single crystals.[4] This provides a way to produce high performance Pb-free piezoelectrics. It implies that $BaTiO_3$, so far regarded as "inferior" piezoelectrics, may show outstanding electrostrain effect if using this electrostrain mechanism. For applications it is very important if similar effect can be achieved in polycrystals/ceramics but such possibility has not been explored. In this letter we investigate such electrostrain behavior in Mn-doped $(Ba,Sr)TiO_3$ ceramics. Experimental results demonstrate that our principle is applicable to ceramics. A large recoverable nonlinear strain of about 0.12%–0.15% under a field of 3 kV/mm can be obtained. This value exceeds that of conventional hard PZT piezoelectric ceramics.

First, we will briefly introduce this mechanism for large electrostrain effect. It is based on a reversible domain-switching process. Electric-field-induced 90° domain switching is known to be able to generate huge strain, as it involves the exchange of nonequal crystalline axis.[5] However, such a huge electrostrain effect is normally irrecoverable (i.e., cannot reappear under field cycles), thus renders the effect useless. This is because domain switching is intrinsically an irreversible effect due to the energetic equivalence of different domain states.[4] However, our mechanism[4] utilizes a universal "symmetry-conforming principle" of point defects (defect symmetry principle) to generate a restoring force for domain switching and consequently realize a reversible domain switching.[4,6–8] This principle was first proposed in ferroeleastic/martensite[6–8] and explained the reversible domain-switching phenomena in aged ferroelastic/martensitic alloys. Very recently it has been successfully extended to ferroelectrics.[4] The main idea is that point defects in crystals possess a so-far unrecognized "statistical symmetry" which follows the crystal symmetry when in equilibrium.[4,6–8] We shall see that it is this symmetry property of point defects which creates a restoring force for reversible domain switching.

Figure 1 shows the symmetry of equilibrium statistical distribution of point defects in a perovskite ABO_3 lattice, which contains acceptor dopant D^{3+} ions at B^{4+} site. To maintain the charge neutrality, oxygen vacancy V_O will be produced at O^{2-} sites.[9] We define $P_i^{V_O}$ as the conditional probability of finding an oxygen vacancy at site i $(i=1-6)$ next to a defect D^{3+}. When temperature is above the Curie point T_C, the crystal possesses a cubic symmetry as shown in Fig. 1(a). As the six sites $(i=1-6)$ are equivalent to D^{3+} due to the cubic symmetry, it is natural that $P_i^{V_O}$ are the same for site-1, 2,–6; thus the distribution of conditional probability (or equivalently short-range-order parameter) shows a cubic symmetry, which conforms to the cubic crystal symmetry.[4] When temperature is below T_C, the cubic crystal structure changes to polar tetragonal due to the displacement of positive and negative ions along the $\langle 001\rangle$ axis as shown in Fig. 1(b). Now the cubic symmetry of oxygen vacancy does not

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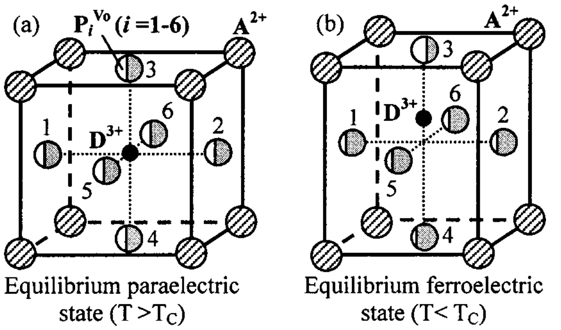

FIG. 1. Symmetry-conforming short-range distribution of point defects in perovskite ABO_3 lattice containing D^{3+} ions at B^{4+} site: (a) equilibrium paraelectric state; (b) equilibrium ferroelectric state. P_i^{Vo} is the conditional probability of oxygen vacancy occupying site-i ($i=1-6$) next to a defect D^{3+}. T_C is the para-ferro-transition temperature. It shows that defect symmetry conforms to crystal symmetry when in equilibrium.

match the polar tetragonal symmetry of the crystal.[4] After given some time (called aging) in ferroelectric state, an equilibrium state is attained, in which distribution of these probabilities shows the same polar tetragonal symmetry, conforming to the polar tetragonal crystal symmetry of the ferroelectric phase, as shown in Fig. 1(b). This is the so-called symmetry-conforming short-range-order principle or in short defect symmetry principle.[4] In this state, the point defect has a tetragonal symmetry and an excess defect polarization $\mathbf{P_D}$ aligning along the direction of $\mathbf{P_S}$.[4] This stable state is schematically illustrated by the symbol shown in Fig. 2(a). In such a stable state [Fig. 2(a)], when electric field **E** is applied along [100] direction perpendicular to $\mathbf{P_S}$, $\mathbf{P_S}$ will switch to the direction of **E** (90° domain switching); however, during such a diffusionless domain-switching process, oxygen vacancy cannot move; thus point defects keep the original symmetry[4] [see Fig. 2(b)]. This is an unstable state according to the defect symmetry principle.[4] Consequently, when **E** becomes zero $\mathbf{P_S}$ will switch back to the original state by the power of point defect symmetry and the associated point defect polarization $\mathbf{P_D}$ [Fig. 2(a)].[4] Such a process generates two important effects: (1) double hysteresis loop (like antiferroelectrics) and (2) huge recoverable strain (with a maximum strain of $c/a-1$).

We chose 1.0 mol % Mn-doped $(Ba_{0.95}Sr_{0.05})TiO_3$ ceramics ($BaSr_{0.05}TiO_3-1Mn$) as our test samples. Mn was added as acceptor dopant. Its valence state is 3+ when sintered at high temperature in air.[10] Oxygen vacancy is simultaneously created by charge compensation.[9] Sr^{2+} was added to lower Curie temperature T_C.[11] According to the Landau theory of phase transition,[11] when temperature is close to T_C, the energy barrier for polarization switching decreases and thus domain switching becomes easier. Such designed samples were sintered by the mixed oxide method at a temperature of 1450 °C for 4 h. The sintered samples were first aged at room temperature for four weeks to establish a stable defect symmetry state as described in Figs. 1(b) and 2(a). Then they were coated with silver electrode on both surfaces.

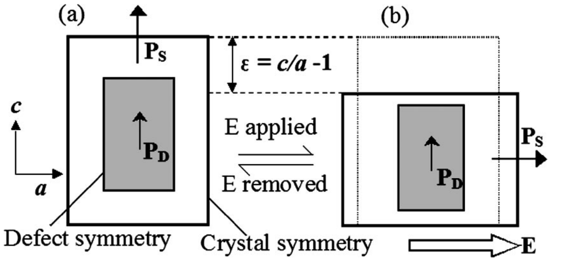

FIG. 2. Point-defect-mediated reversible domain switching from (a) stable state to (b) unstable state generates a large electrostrain of $c/a-1$. $\mathbf{P_S}$ (thick arrow) and $\mathbf{P_D}$ (thin arrow) denote spontaneous polarization and averaged defect polarization, respectively. c and a are the length of c and a axes of the tetragonal ferroelectric unit cell, respectively. Large rectangle represents crystal symmetry and small rectangle represents defect symmetry.

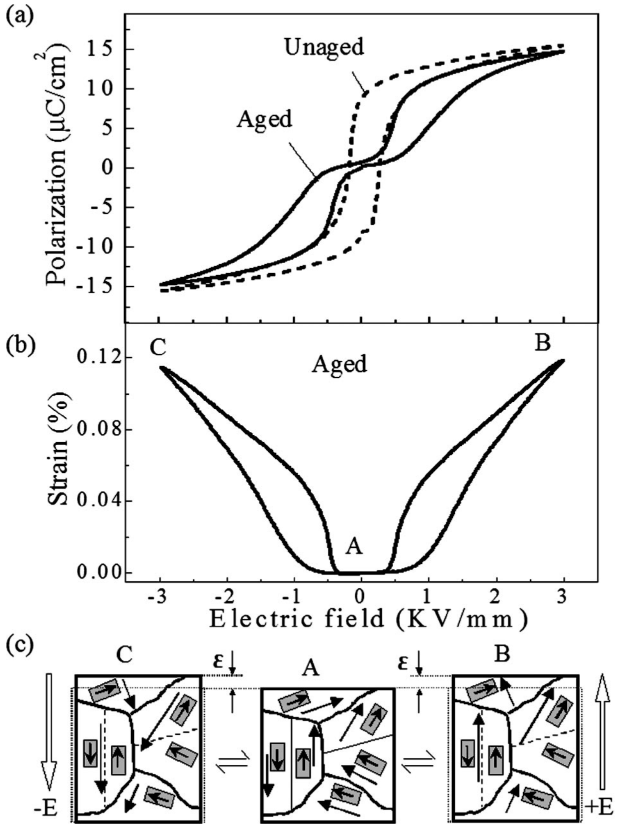

FIG. 3. Aging effect of $BaSr_{0.05}TiO_3-1Mn$ ceramics and microscopic mechanism of the recoverable electrostrain effect: (a) hysteresis loop before and after aging; (b) field-induced electrostrain in aged sample; (c) microscopic mechanism, see Fig. 2 for definition of arrows and rectangles.

Figure 3 showed the measured hysteresis loop and strain as a function of the electric field at room temperature for aged $BaSr_{0.05}TiO_3-1Mn$ sample. It is noted that the aged sample shows an interesting double $P-E$ hysteresis loop (solid line) contrast to the normal hysteresis loop for unaged state (dotted line) [Fig. 3(a)]. With the electric field increasing to 3 kV/mm, polarization of the aged sample increases to 15 $\mu C/cm^2$, and then recovers to zero when electric field decreases to zero. Similar double hysteresis loop in aged ferroelectrics have also been reported.[12] Most importantly, accompanying the double hysteresis loop, the aged sample shows a large recoverable electrostrain of 0.12% under bipolar electric field [Fig. 3(b)]. This strain value is close to the theoretical value for ceramics associated with domain switching, which is known to be 0.368% for $BaTiO_3$.[13] The microscopic process underlying this interesting behavior of ceramics can be well understood by the illustration of Fig. 3(c). The basic mechanism for the reversible domain switching for the aged polycrystal (ceramics) case is the same as the abovementioned single crystal case (Fig. 2). The only difference is that ceramics are composed of many randomly

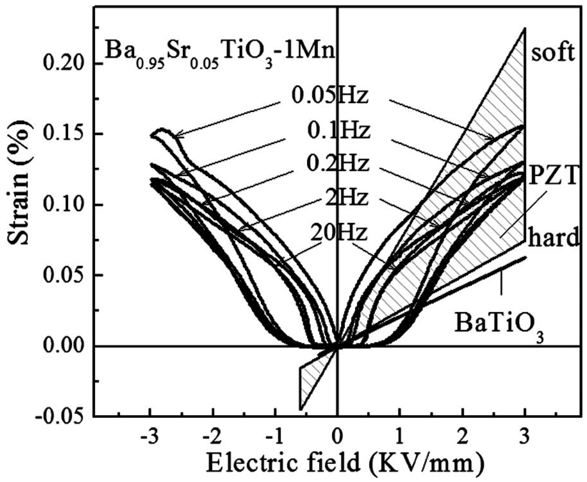

FIG. 4. Comparison of the nonlinear recoverable electrostrain in $BaSr_{0.05}TiO_3-1Mn$ ceramics with linear piezoelectric strain of $BaTiO_3$ and PZT ceramics (shaded area). The recoverable strain effect is stable over a wide field frequency range.

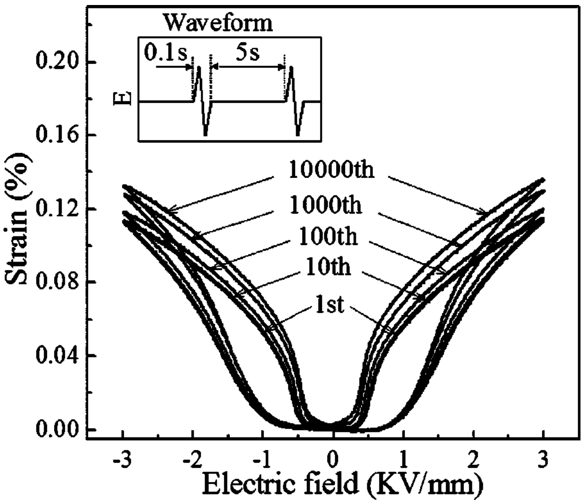

FIG. 5. Cycle dependence of electrostrain for $BaSr_{0.05}TiO_3-1Mn$ ceramics at 3 kV/mm electric field. Perfect recoverability is achieved even after 10 000 cycles. The waveform of electric field is shown in the inset.

oriented grains, which reduce the maximum attainable electrostrain. This explains the double hysteresis loop and the recoverable strain versus electric field in Fig. 3.

It should be stressed here that the point-defect-mediated recoverable electrostrain is a nonlinear effect, being different from the linear piezoelectric effect but the strain level shown in Fig. 4 exceeds not only conventional linear piezoelectric strain of $BaTiO_3$ ceramics themselves, but also the piezoelectric strain of hard PZT ceramics; it even approaches the strain level of soft PZT ceramics. As can be seen from the Fig. 4, $BaSr_{0.05}TiO_3-1Mn$ ceramics show a recoverable electrostrain of 0.12%–0.15% under 3 kV/mm field, which exceeds that of piezoelectric $BaTiO_3$ (0.063%) and hard PZT (0.075%[14]), and is close to soft PZT (about 0.2%[14]). Also this effect is stable down to a low frequency of 0.05 Hz. Besides the stability, this effect shows perfect recoverability even when the applied electric field reverses its direction. By contrast, the piezoelectric effect can only be used in a limited range under negative electric field, being less than 1 kV/mm. For the abovementioned advantages, the point-defect-mediated recoverable electrostrain effect in $BaSr_{0.05}TiO_3-1Mn$ ceramics demonstrates a potential for applications in nonlinear actuators.

It can be noted from Fig. 4 that with field frequency decreasing, the strain level increases but recoverability becomes weaker. This may be due to the migration of a part of point defects during the slow cycling process, which align along the direction of applied electric field. As the result, the remaining point defects that resist domain switching become fewer. Consequently, domain switching becomes easier. This corresponds to a smaller coercive field. Besides, domain switching will become more complete and this contributes to a larger strain level.

We further investigated the stability of the recoverable electrostrain against field cycling. The test sample was also $BaSr_{0.05}TiO_3-1Mn$. The waveform of the electric field was shown in Fig. 5. It showed that the electrostrain has a good recoverability even after 10 000 cycles at 3 kV/mm electric field. This result further supports the application possibility of our mechanism. Interestingly, we found that the strain level increases with increasing number of cycles. This phenomenon can be explained as follows. Cycling may assist some point defects (defect dipoles) to align along field direction (from other directions), thus creates a weakening of resistance to domain switching. By the same reason as discussed for frequency effect, strain level also increases. Therefore, it can be said that both lower frequency and field cycling enhance domain mobility.

In conclusion, based on the defect symmetry principle, a large nonlinear recoverable electrostrain of about 0.12%–0.15% was obtained in $BaSr_{0.05}TiO_3-1Mn$ ceramics. It exceeds that of conventional piezoelectric hard PZT ceramics. Moreover, this electrostrain effect is stable down to a low frequency of 0.05 Hz and shows good recoverability even after 10 000 fatigue cycles. These results indicate the potentiality of this electrostrain mechanism for applications as nonlinear actuators.

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