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Large digital-characterized electrostrain in Mn-doped (Pb,Sr)TiO_3 electro-shape-memory ceramics

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In the present letter, we report that through a reversible domain switching mechanism, a large electro-shape-memory effect (up to 0.23% under the electric field of 5 kV/mm) is achieved in the aged Mn-doped (Pb,Sr) TiO_3 ceramics. We also provide the microscopic understanding on the relationship between the strain (ε) and field (E) curve with aging phenomenon. Different from the common analogue response (linear converse piezoelectric effect), such electrostrain exhibits a digital characteristic and consequently enables a promising "on-off" application. Owing to the domain switching nature, the key parameters (e.g., maximum strain, coercive field and working temperature range) of the present electrostrain can be customized by changing the ratio of Pb/Sr and thus the ratio of c/a to facilitate the possible practical applications. © *2011 American Institute of Physics*. [doi:10.1063/1.3632079]

Electro-shape-memory ceramics exhibit a shape change to a predefined state upon a change of an electric field. Such materials provide a good solution to the "quick and slim" actuator applications since they guarantee a fast response (e.g., kHz or even higher, compared with the temperature-shape-memory alloys) and their required driven field can be easily applied through very fine guide wires (compared with the bulky magnets required by magnetic-shape-memory materials).[1–3] Traditionally, there exist three categories of electro-shape-memory ceramics classified by different mechanisms. The major part is piezoelectrics, which achieve memory effect in the pre-poled ferroelectrics by ionic shift (normally 0.1%–0.2%).[4] In addition, some relaxor ceramics (e.g., $Pb(Mg_{1/3}Nb_{2/3})O_3$) present electrostriction by transition between normal ferroelectric states and random arrangement of micro-domain states.[5–7] Besides, very few ceramics [e.g., $(Pb,Nb)(Zr,Sn,Ti)O_3$] can also generate electrostrains by switching between antiferroelectric and ferroelectric states within very narrow composition range and temperature range.[8–10]

Here, we report large digital-like electrostrains (up to 0.23%) which were generated by a different mechanism besides the above conventional three. Such electrostrains are achieved through an aging-induced reversible domain switching mechanism in the acceptor-doped (Pb,Sr)TiO_3 ceramics. As only domain switching is concerned to contribute to the electrostrain (with the strain value depending on the difference between non-equal crystallographic axes, e.g., (c/a-1) for ferroelectrics with tetragonal symmetry), it is obvious that such mechanism can be applied to wide range of ferroelectrics to generate large electrostrains within wide temperature range. Furthermore, several key parameters of such electrostrains can be customized to satisfy various applications, e.g., magnitude of electrostrain, coercive field, and usage temperature range, by adjusting the c/a ratio in the (Pb,Sr)TiO_3 system. The present work not only theoretically provides deeper understanding on the new method to generate large electrostrain (by aging induced recoverable domain-switching mechanism) but also demonstrate a promising system to satisfy the "on-off" applications.

Figs. 1(a)–1(d) illustrate the recoverable domain-switching mechanism.[11–14] During "aging" process, the mobile defects migrate to consist with the crystal symmetry. At the same time, defect polarization (P_d) is generated and aligns along the same direction as spontaneous polarization (P_s), [Figs. 1(a) to 1(b)]. When an electric field E is applied on the aged samples, P_s reorientation happens while P_d keeps still during such a diffusionless process [Figs. 1(b) to 1(c)]. Once E is removed, P_s will switch back to its original state by the power of P_d [Figs. 1(c) to 1(b)]. Macroscopically, non linear recoverable electrostrain ε is expected associated with such reversible domain switching process [Fig. 1(d)]. It can be noted that the above mechanism is different from the most widely applied linear piezoelectric principle (Fig. 1(e)). Since it originates from the domain switching process, it has to overcome a threshold at the very beginning and then suffers an abrupt strain change. Such digital-like responds will enable "on-off" applications. Also importantly, it is applicable to all the mobile-dopant-contained ferroelectrics that can find application in a wide range of ferroelectric candidates. Such feature also precedes the other two strain mechanisms. One merely refers to some relaxor ferroelectrics and generates S-curved electrostrains by transition between normal ferroelectric states and relaxor states as Fig. 1(f) shown. The other mechanism can be applied to a few antiferroelectrics and generate similar digital-like strain by switching between antiferroelectric and ferroelectric states as Fig. 1(g) shown. But such mechanism only works within narrow concentration and temperature range.

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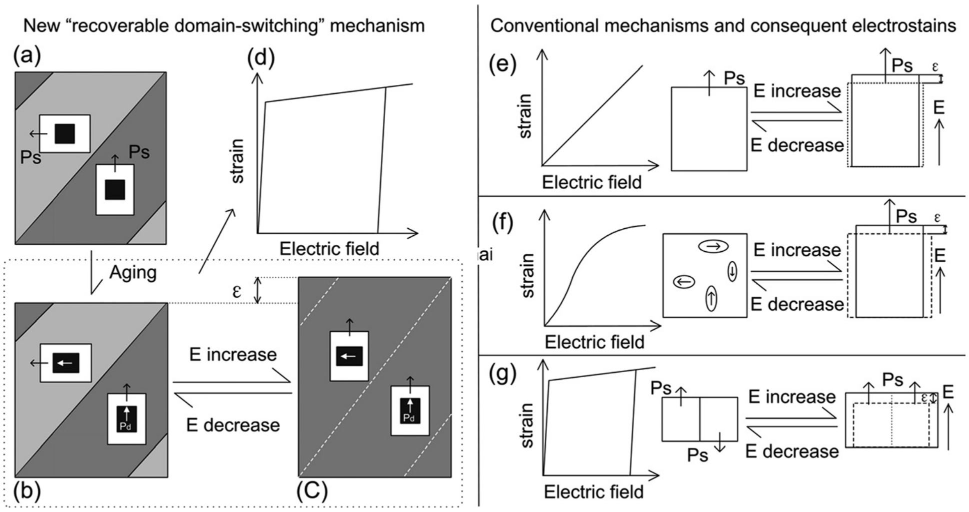

FIG. 1. Recoverable domain switching mechanism for electrostrain [(a)-(d)] comparing with the conventional three and their resultant strain [(e)-(g)]. (a) Fresh ferroelectric state where defect symmetry remains cubic. P_s represents the spontaneous polarization. (b) After aging, defect symmetry adopts a polar tetragonal symmetry (with a defect dipole P_d). The large rectangle represents crystal symmetry while the small black rectangle represents defect symmetry. (c) On increasing electric field E, P_s rotates but P_d keeps the original orientation; this unswitched P_d provides a restoring force for reverse domain switching to (b). (d) As a macroscopic phenomenon, digital like electrostrain is generated. (e) Linear piezoelectric effect based on ionic shift. (f) Switching between relaxor and normal ferroelectric state and its consequent S-curved electrostrain. (g) Switching between anttiferroelectric and ferroelectric state and the consequent strain.

In the present study, we chose 1.0 mol% Mn doped $(Pb_xSr_{1-x})TiO_3$ as our test samples (abbreviate as P100xST-1Mn). Aging was done below T_C of each sample to establish an equilibrium defect state.

Fig. 2 shows the experimental results of the hysteresis loop and electrostrain under the frequency of 1 kHz for the aged P50ST-1Mn sample. Different from the unaged sample which exhibits the normal loop (dotted line), the aged sample shows the interesting double hysteresis loop as shown by solid line in Fig. 2. At the same time, its saturation polarization decreases to 25 μC/cm^2 while the coercive field increases to 2.50 kV/mm compared with unaged sample. This suggests that after "aging" treatment, mobile defects indeed generate an intrinsic force which acts as the resistance in forward process while restoring force in the backward process during the reversible domain switching. More interestingly, as another macroscopic phenomenon, the aged P50ST-1Mn ceramic shows a large recoverable electrostrain of 0.23%. It should be noted here that the electrostrain of P50ST-1Mn, which is based on the reversible domain switching, is fundamentally different from the conventional linear piezoelectric effect. Compared with the similar aging-induced recoverable electrostrain effect reported in $BaTiO_3$-based ceramics,[13] PST-Mn ceramic has the highly abrupt jump at a critical field. Such feature may enable wide range for on/off applications.

From the mechanism described above, such digital like electrostrain arising from the non-180° reversible domain switching strongly depends on c/a, thus properties for given application will be achieved with appropriate c/a. In the present PST system, c/a can be easily adjusted by changing Curie temperature Tc, i.e., changing Pb/Sr ratio. Fig. 3 shows the dielectric permittivity thermograms and XRD spectrums specialized

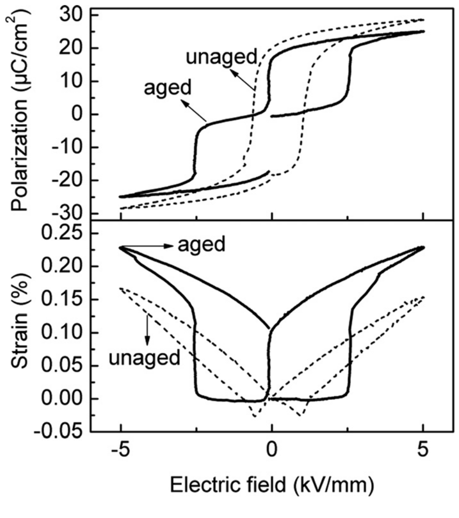

FIG. 2. Hysteresis loops and electrostrain (before and after aging) for the 1 mol% doped $(Pb_{0.5}Sr_{0.5})TiO_3$ ceramic. The frequency for measurement is 1 kHz.

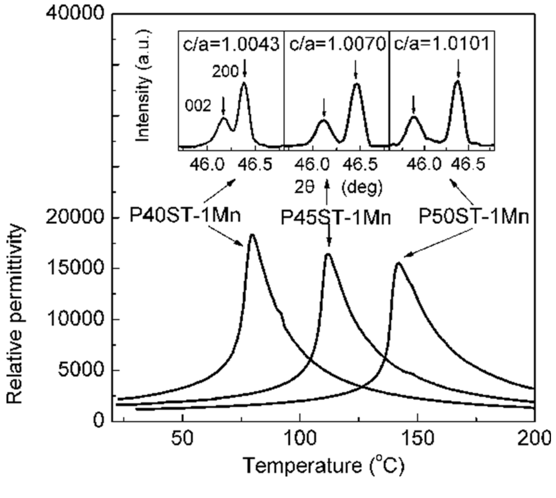

FIG. 3. Dielectric permittivity vs. temperature relations and XRD profiles specialized in {200} for P40ST-1Mn, P45ST-1Mn, and P50ST-1Mn, respectively.

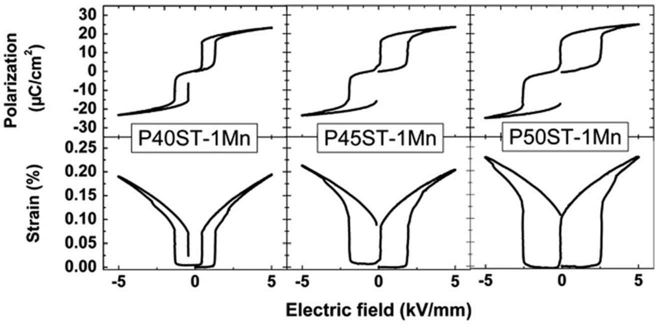

FIG. 4. Hysteresis loops and electrostrain curves for P40ST-1Mn, P45ST-1Mn, and P50ST-1Mn, respectively. The frequency for measurement is 1 kHz.

in {200} of the ceramic samples with different Pb/Sr (P40ST-1Mn, P45ST-1Mn, and P50ST-1Mn) under 1 kHz. Here, the intensity ratio of the split peaks for {200} with 1:2 characterizes a tetragonal structure and c/a is calculated by such characteristic splitting. It is obvious that on increasing Pb/Sr, the Tc increases from 72 °C to 142 °C. At the same time, the tetragonality enhanced; c/a increases from 1.0043 to 1.0101.

Fig. 4 shows the hysteresis loops and electrostrain curves from the ceramics with different Pb/Sr ratio. It is clear that on increasing the Pb/Sr ratio (i.e., increasing c/a), the magnitudes of the electrostrains became larger (the maximum strain in theory can be easily calculated to be (c/a)-1, where c and a are the length of c and a axes, respectively, of the tetragonal ferroelectric phase in the PST system). However, it should be stressed that the strain value did not increase proportionally to the c/a ratio by changing Pb/Sr ratio (the strain is 0.20%, 0.21%, and 0.23%, respectively, in P40ST-1Mn, P45ST-1Mn, and P50ST-1Mn samples). The reason is that, increased c/a has negative effects on domain-switching related electrostrain. First, larger c/a will introduce larger energy barrier between different equivalent polarization states according to the Landau theory and consequently limit the population of switchable domains. Second, c/a is the driving source for forming P_d. Larger c/a will introduce larger P_d which also play as a resistance force for initial domain switching process and increase coercive field. Hence, larger c/a may block domain switching in a certain extent and lead to larger coercive field as well as smaller polarization. This is verified by the experimental data that the coercive field increases from about 1.3 kV/mm to 2.5 kV/mm with increasing the Pb/Sr ratio.

TABLE I. Properties of the ceramics with different Pb/Sr ratio.

	Tc (°C)	c/a	Pmax (μC/cm^2)	Ec (V/mm)	Strain (%)
P40ST-1Mn	79.2	1.0043	23.38	1328	0.20
P45ST-1Mn	112.1	1.0070	23.60	1910	0.21
P50ST-1Mn	142.1	1.0101	25.02	2566	0.23

As a summary, the properties of the ceramics with different Pb/Sr ratio were given in Table I. A large electrostrain can be achieved in all the different Pb/Sr ratio samples, while with the different transition temperature. This indicates a wide adjustable temperature range of the large recoverable electrostrain effect.

In conclusion, we introduce a electro-shape-memory system Mn doped (PbSr)TiO_3 ceramics exhibiting large electrostrain (up to 0.23%) and provide the microscopic understanding on the ε–E aging phenomenon. The present electrostrain possess digital-like characteristic which is different from the conventional linear converse piezoelectric effect and that of the previous reported $BaTiO_3$ based ceramics which arising from the same reversible domain-switching mechanism. These results may provide new insight into how to develop on/off electro-shape-memory materials in a wide range of ferroelectrics.

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