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In situ observation of thermally activated domain memory and polarization memory in an aged K^+-doped (Ba, Sr)TiO_3 single crystal

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Abstract
Different ferroelectric domains are degenerate states of the same ferroelectric phase; thus they are energetically equivalent and, in principle there exists no preference for a particular domain pattern. However, the existence of point defects is considered to stabilize certain preferential domain states. In order to study the temperature violation on such stabilized domains, we performed *in situ* observation on an aged K^+-doped (Ba, Sr)TiO_3 single crystal and found that both the domain configuration and polarization state can be memorized after experiencing a thermally activated ferro–para–ferro transition cycle, as manifested by a reappearance of the same domain pattern and double P–E hysteresis loop. In contrast, after the sample was aged in the paraelectric state (>10 min), these memory effects disappeared. The above memory effects are considered to originate from the interaction between point defects and the crystal symmetry driven by a symmetry-conforming tendency of point defects. Such a mechanism suggests that the memory effects are relevant to the existence of acceptor dopant and associated mobile oxygen vacancies, and they are not restricted to a particular dopant. Thus similar memory effects are expected to exist in a wide range of ferroelectric materials with acceptor doping.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

For over half a century ferroelectric materials have become an indispensable part of modern technology, owing to their rich ferroelectric, piezoelectric and dielectric properties [1]. These important properties are largely controlled by their ferroelectric domains; thus understanding the behavior of ferroelectric domains has been a central issue for ferroelectric research [2–8].

Ferroelectric domains (i.e. regions of uniform spontaneous polarization) are formed as a result of a symmetry-lowering ferroelectric transition at the Curie temperature. For an ideal ferroelectric crystal, different domain states are crystallographically equivalent with respect to the high-symmetry paraelectric phase, and thus are energetically degenerate [3, 5]. Because of the degeneracy of the ferroelectric domain states, a ferro–para–ferro transition cycle or an electric-field cycle cannot guarantee the restoration of the previous domain configuration. As a result, there is no memory of the preexisting domain state. Consequently, a normal single polarization–electric field (P–E) hysteresis loop is usually observed in a ferroelectric state, reflecting the bistability in the polarization state [6, 8].

Nevertheless, crystalline solids invariably contain some lattice defects (dopant, vacancy or impurity) [9]. With the existence of point defects, especially the acceptor dopants, the aged ferroelectric crystal is considered to show certain preferential polarization states, manifested by the appearance of a double P–E hysteresis loop in the unpoled sample [6, 8]. It is generally agreed that such behavior can be attributed to a gradual stabilization of ferroelectric domains by defects during the aging process [6–8, 10, 11]. Then, the study of the effect of temperature/external field violation on such stabilized domain is of importance for both fundamental interest and practical applications [7, 8, 12–14]. Tan *et al* have studied the thermal effects on the P–E loop in K^+-doped PZT (lead zirconate titanate) ceramics, and showed that aging below T_C results in double P–E loop while annealing above T_C rectifies the double P–E loop into a normal one [13]. A very recent phase field simulation study [7, 8] has shown the recovery of the domain pattern after a rapid heating/cooling transition cycle, due to short-range ordering of charged point defects. In the present study, we performed *in situ* observations for such a process on a K^+-doped (Ba, Sr)TiO_3 single crystal, which had been previously well aged in the ferroelectric state. We found that both the original domain pattern and double P–E loop can be fully restored after experiencing a rapid ferro–para–ferro heating/cooling cycle. And the above memory effects disappeared after the specimen was aged in the paraelectric state. We attempt to understand such results by considering the interaction between point defects and the crystal symmetry.

2. Experimental procedure

The K^+-doped (Ba, Sr)TiO_3 single crystal used in the present study was grown by the KF flux method at about 1200 °C [15]. The as-grown samples were annealed at 1000 °C for 10 h to remove the F^- so that the remaining K^+ was on the Ba^{2+} site as an acceptor dopant and the oxygen vacancy could be created by charge compensation [15]. The Ba/Sr ratio was analyzed to be about 85/15 and the concentration of K^+ was analyzed to be about 1.4 mol% by using the x-ray fluorescence analyzer XRF-1800 from Shimizu Corporation. Sr^{2+} was added to lower the Curie temperature, so that the oxygen vacancy diffusion in the high-temperature phase was not too fast to detect [16]. The Curie temperature of the single crystal, determined by the permittivity versus temperature curve, is about 76 °C. The single crystal sample for optical microscopy was polished on both sides to less than 100 μm thick. And the samples for polarization measurement were coated with silver electrodes on both sides. Ferroelectric hysteresis loops were measured with a ferroelectric tester (Radiant Workstation) at 10 Hz.

3. Results

First, we performed *in situ* domain observation during a ferro–para–ferro transition cycle with a K^+-doped (Ba, Sr)TiO_3 single crystal, shown in figure 1. To remove the possible surface stress after polishing, the polished sample was initially annealed at 200 °C for 2 h and cooled with a furnace to room temperature at a very slow rate of 50 °C h^{-1}. Then the sample was held at room temperature (RT) for one month to establish a stable well-aged ferroelectric state. It is characterized by a typical domain pattern (figure 1(a)) of tetragonal symmetry. When the sample was heated up to above T_C (90 °C), the domain pattern disappears in the paraelectric state (figure 1(b)), as expected. At this temperature (T_C + 14 °C), there is no residual domain over the whole sample, thus it reaches the paraelectric state totally. Without holding in the paraelectric state, we cooled the sample down to the ferroelectric state and found that the newly formed domain pattern (figure 1(c)) is fully identical to the original domain pattern shown in figure 1(a), i.e. the aged domain configuration can be memorized after a rapid heating and cooling cycle. Such a domain memory effect shows good agreement with the recent phase field simulation results [7]. However, if the sample was heated up to above T_C and then held in the paraelectric state for a long time (>10 min) (figure 1(d)), on subsequent cooling to the ferroelectric state, a completely different domain pattern is formed (figure 1(e)), indicating that the system loses the memory of the original ferroelectric domain pattern.

To explore what happens with the macroscopic properties during the above ferro–para–ferro transition cycles, we studied the evolution of the P–E loop of the same aged K^+-doped (Ba, Sr)TiO_3 single crystal during the same transition/aging cycles. The results are shown in figure 2. The starting sample exhibits a double P–E loop (figure 2(a)), which corresponds to a well-aged ferroelectric state [6, 8, 12]. When the sample was heated to above T_C, the P–E loop became almost a line (figure 2(b)), characterizing a paraelectric state. Without holding, we quenched the sample to the ferroelectric state (RT), and found it exhibits the same double P–E loop (figure 2(c)) as the previous one (figure 2(a)). This indicates that the previous polarization state of the ferroelectric phase was memorized after this rapid heating and cooling cycle. This polarization memory effect (figure 2(a) versus figure (c)) is consistent with the domain pattern memory effect (figure 1(a) versus figure (c)). Similar to the vanishing of the domain pattern memory effect, after the sample was held in the paraelectric state for a long time (figure 2(d)), the polarization state could no longer memorize its initial state, as evidenced by the appearance of a normal P–E loop (figure 2(e)) when cooling to RT. Clearly, such a rectangular P–E hysteresis loop corresponds to the new domain pattern shown in (figure 1(e)).

It is obvious that these memory effects are dependent on the holding process in the paraelectric phase, which is known as thermally activated de-aging. In order to control the domain and polarization memory effects, it is important to clarify the thermally activated de-aging process in both temperature and time scales. It has been reported that the thermally activated de-aging process takes 500 s to finish at the temperature 33 °C higher than T_C in Mn^{3+}-doped $(Ba_{0.80}Sr_{0.20})TiO_3$ ceramics [16]. The time scale in the present study coincides with such a time scale, that is, the domain memory and polarization memory effects disappear when the de-aging process at the paraelectric phase is longer than 600 s. Studies on the kinetics of the thermally activated de-aging process have shown that the de-aging behavior is qualitatively the same at different temperatures, but the aging becomes

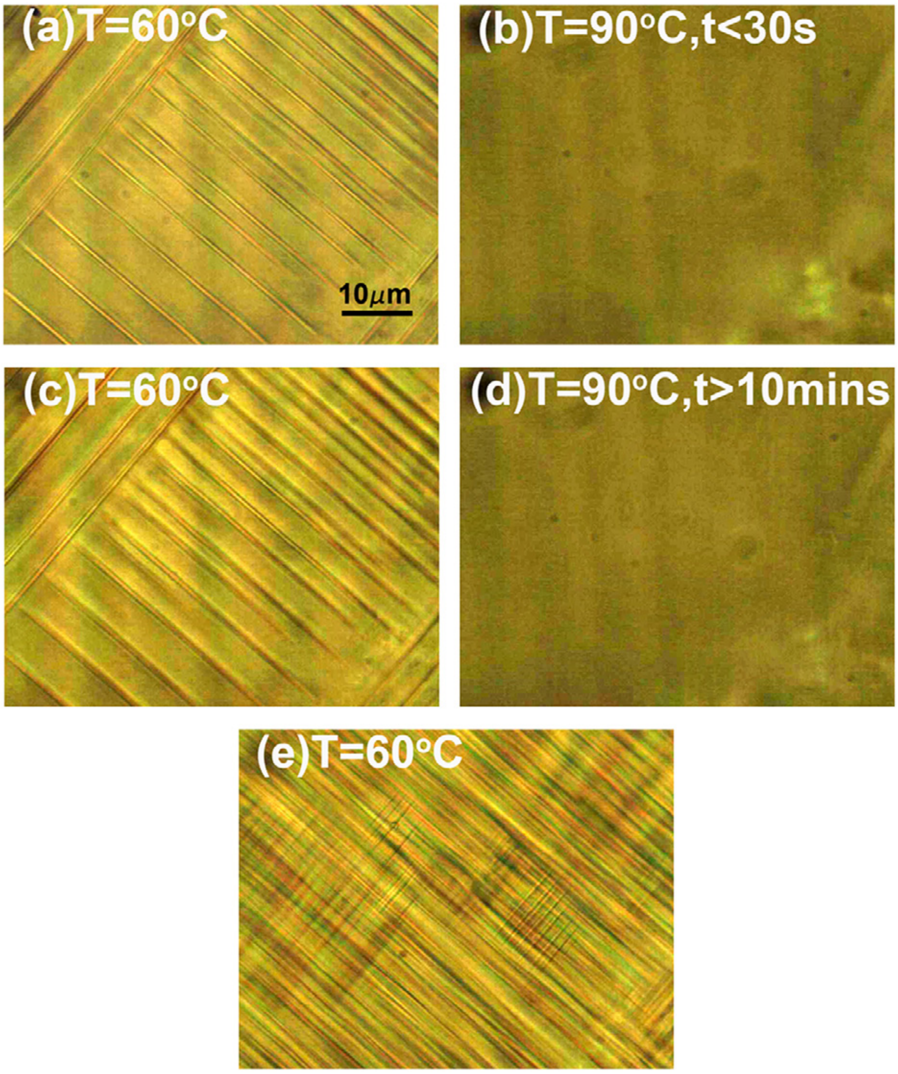

Figure 1. *In situ* optical microscopy of domain pattern evolution of K^+-doped (Ba, Sr)TiO_3 single crystal. (a) The domain pattern of the well-aged ferroelectrics. The sample was heated up to (b) the paraelectric phase and cooled down to (c) the ferroelectric phase. Then the sample was heated up again to (d) the paraelectric phase and held, following by cooling down to (e) the ferroelectric phase.

faster with increasing aging temperature [16]. The temperature dependence of de-aging time can be presented as an Arrhenius-type process with characteristic activation energy [16, 25]. This indicates that the higher de-aging temperature and longer de-aging time will result in easier vanishing of those memory effects.

4. Discussion

The above *in situ* experimental observations show that both domain pattern and polarization state can be memorized after the specimen experiences a rapid ferro–para–ferro heating/cooling cycle; while these memory effects disappear when the specimen is well aged in the paraelectric state. Then, the central question in the following is how to understand the observed phenomena.

As is well known, many phenomena related to aging in ferroelectrics have been understood by considering the interaction between defect dipoles and crystal structure [6–8, 10–12, 17, 18]. Nowick and Heller have discussed in detail the symmetry aspects between defects and crystal, and also the time dependence of defect orientation once the symmetry conformity is violated by temperature or external field [19]. Robels and Arlt also have acknowledged this important idea in dealing with the ferroelectric aging phenomena [10, 17]. With this rich knowledge, Ren *et al* have explained the long-standing puzzle (i.e. rubber-like behavior) in martensitic alloys by considering the short-range ordering of point defects in crystal (termed as 'symmetry-conforming short-range ordering principle' (SC-SRO)) [20]. By applying such a principle in ferroelectrics, a large recoverable electrostrain (∼0.75%) is achieved in aged $BaTiO_3$ single crystal [12]. The main idea of the SC-SRO principle is that the symmetry of short-range order distribution of point defects tends to follow the crystal symmetry when in equilibrium (see details in [9]). In the equilibrium ferroelectric state (i.e. aged ferroelectric state), the polar crystal symmetry will lead to

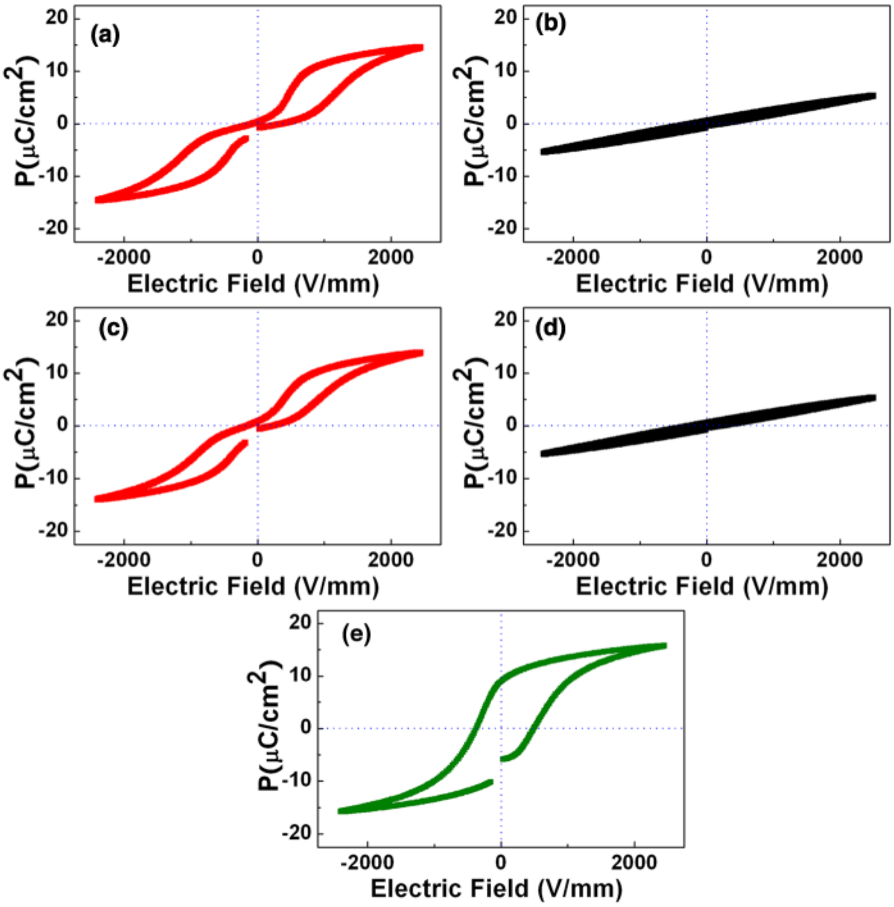

Figure 2. The P–E loop evolution of K^+-doped (Ba, Sr)TiO_3 single crystal. (a) The double loop of the well-aged ferroelectrics. The sample was heated up to (b) the paraelectric phase and cooled down to (c) the ferroelectric phase with a double loop. Then the sample was heated up again to (d) the paraelectric phase and held, followed by cooling down to (e) the ferroelectric phase with a normal loop.

a polar defect SRO distribution and hence creates a defect polarization $\mathbf{P}_D$ aligning along the spontaneous polarization $\mathbf{P}_S$ direction [6, 12]. On the other hand, in the equilibrium paraelectric state (i.e. aged paraelectric state) both the crystal symmetry and the defect SRO distribution are cubic; thus no defect polarization $\mathbf{P}_D$ exists [16].

By using this SC-SRO principle, we try to understand the above experimental observations. Figure 3(a) shows that in the well-aged (equilibrium) multi-domain ferroelectric phase, the defect polarization $\mathbf{P}_D \parallel \mathbf{P}_S$ holds in each domain [21, 22]. When such stable domains are switched by an electric field, domain switching occurs abruptly (without diffusion) with $\mathbf{P}_S$ following the external electrical field direction. However, based on Warren *et al*'s results [23] and Tan *et al*'s experimental results [13], the $\mathbf{P}_D$ cannot be rotated in such a diffusionless process, since the reorientation of $\mathbf{P}_D$ involves the oxygen vacancy migration. This unswitchable $\mathbf{P}_D$ provides a restoring force or reverse internal field favoring a reverse domain switching when the electric field is removed, so a double P–E loop is observed [6, 8]. On heating, the specimen undergoes an abrupt symmetry change at T_C from tetragonal to cubic ($\mathbf{P}_S = 0$). During this process, $\mathbf{P}_D$ remains unchanged, because the change of defect symmetry from tetragonal to cubic requires some time to finish as it involves the short-range migration of oxygen vacancies [13, 23]. Thus, this paraelectric state (figure 3(b)) is of cubic crystal symmetry embedded with a tetragonal defect symmetry. When this paraelectric state is immediately cooled down to the ferroelectric phase, the defect polarization $\mathbf{P}_D$ provides an internal field favoring the formation of previous ferroelectric domains so that $\mathbf{P}_D$ follows the $\mathbf{P}_S$ direction in each ferroelectric domain to minimize the total system free energy. Therefore, the same domain pattern reappears (figure 3(c) versus figure (a)); such a domain pattern is also stable with respect to electrical field cycles so a double P–E loop reappears. That is why we observed the domain pattern memory and polarization memory effects.

However, long time aging in the paraelectric state enables the defect symmetry to change from tetragonal to cubic to follow the cubic crystal symmetry through oxygen vacancy migration. As a result, defect polarization $\mathbf{P}_D$ finally vanishes (figure 3(d)) [16]. When such an aged paraelectric phase is cooled down to the ferroelectric state (figure 3(e)), there is no preference of the previous domain pattern or polarization state. As a consequence, a new energetically equivalent domain pattern will appear and it is characterized by a normal P–E loop. That is why we observed the disappearance of domain pattern memory and polarization memory effects.

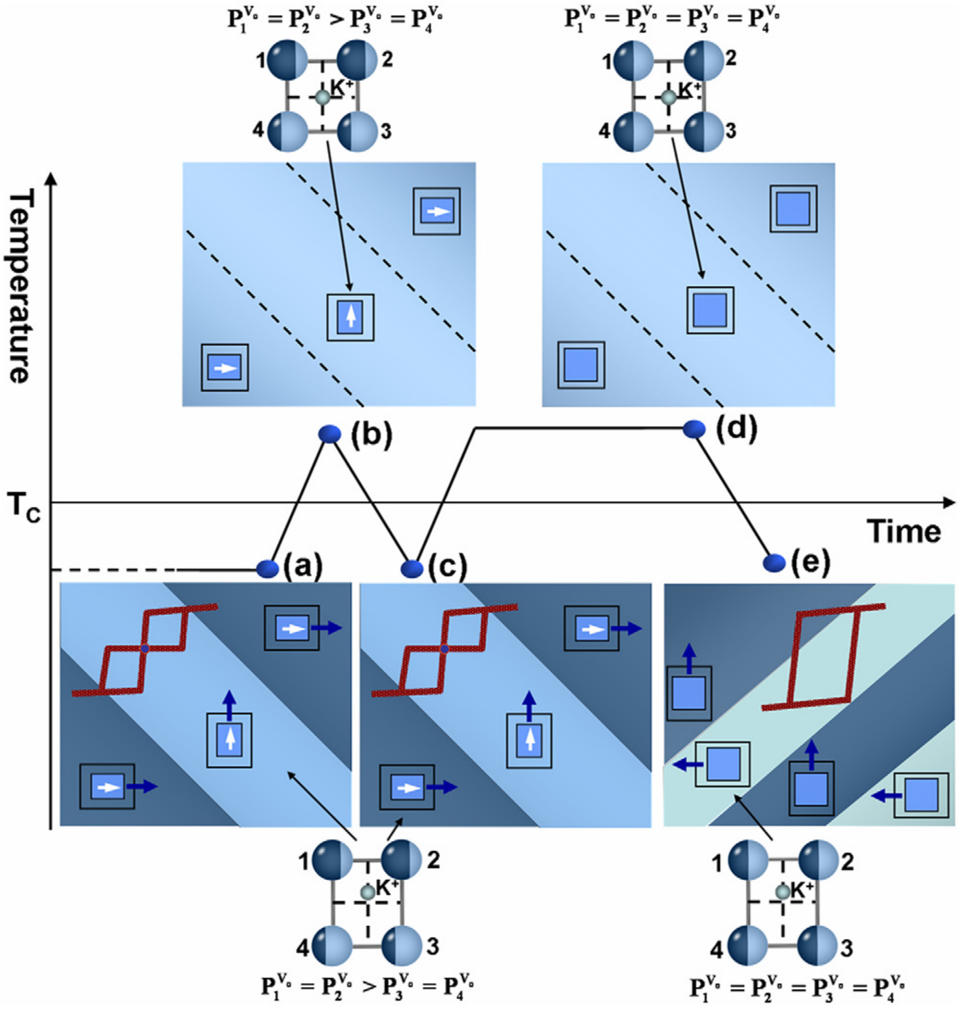

Figure 3. A microscopic explanation for the memory effects; (a) and (c) equilibrium ferroelectric state with polar tetragonal defect symmetry. (b) Non-equilibrium paraelectric phase adopting the polar tetragonal defect symmetry. (d) Equilibrium paraelectric state with non-polar (cubic) defect symmetry. (e) Non-equilibrium ferroelectric state with cubic defect symmetry. Besides each domain is the symmetry-conforming short-range ordering of point defects in a perovskite ABO_3 lattice containing K^+ ions at the A^{2+} site. For simplicity, only the (100) plane of the structure is shown. $P_i^{V_o}$ is the conditional probability of finding an oxygen vacancy at site $i\,(i = 1, 2, 3, 4)$ around an acceptor ion (K^+). Within each domain structure is the symbolic representation of its crystal symmetry (large square or rectangle) and defect symmetry (small square or rectangle), respectively. The large and small arrows represent respectively the spontaneous polarization $\mathbf{P}_S$ and the defect polarization $\mathbf{P}_D$ associated with the polar distribution of charged point defects.

Up to now, we have only considered a particular acceptor dopant K^+ at the A site, obeying the SC-SRO principle to understand these memory effects. However, the SC-SRO principle is applicable to any other acceptor dopants in the ferroelectrics [6, 12] and it works well in both single crystals [12, 15] and polycrystals [16], because only symmetry is of relevance. Thus it is considered that the appearance of the above memory effects is relevant to the existence of acceptor dopant and associated mobile oxygen vacancies, and it should not be restricted to the single crystal samples or rely on a particular dopant. Therefore, similar memory effects are expected in a much wider range of acceptor doped ferroelectric materials.

It should be noted that the aged ferroelectric state can be 'erased' by holding and quenching from a temperature higher than T_C (in the present study) or by cycling with an electric field [11, 24, 25]. The de-aging of hard PZT by electric field is well documented [11]. A very recent study has shown that the de-aging by electric field is mainly ascribed to the short-range migration of oxygen vacancies, but also probably ascribed to the long-range charge drift since the quasi-dc cycling field provides the external driving force to destroy the electrostatic order [24, 25]. However, for the thermally activated de-aging process, the driving force for the defect dipole reorientation is only the minimization of their elastic and electrostatic energies. Thus, only the short-range migration of point defects is considered to be necessary to complete the thermal activated de-aging process in the present study.

Interestingly, similar domain memory effects have been reported in an aged Au-49.5 at.% Cd martensitic alloy during a thermally activated martensite–austenite–martensite cycle and are also ascribed to the interaction between point defects and crystal symmetry [9]. A similar domain memory effect in martensitic alloys results in the 'ageing induced two way shape memory effect', which can find applications as time-sensitive actuators [9]. In ferroelectric materials, since the memory effects are closely related to time and temperature, it is considered that such effects may find potential applications as time or temperature-sensitive switches.

Finally, we point out here that the rejuvenation effect of ferroelectric fatigue [26], which shows the recovery of the spontaneous polarization as well, is different from our results related to ferroelectric aging or de-aging. The difference is that ferroelectric aging involves a short-range diffusion process [6], while fatigue involves a long-range diffusion process [27].

5. Summary

In summary, we have carried out *in situ* observations on an aged K^+-doped (Ba, Sr)TiO_3 single crystal and found that both domain pattern and polarization state can be memorized after a rapid thermally activated ferro–para–ferro transition cycle; in contrast, when the samples are aged in the paraelectric state for a long time, the memory effects disappear. Such memory effects in ferroelectrics bear a striking similarity to those in martensitic alloys, suggesting a common origin for the phenomena. We suggest that the underlying mechanism is a memory of short-range order symmetry of point defects, resulting from the interaction between point defects and the crystal symmetry.

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