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Aging-induced domain memory in acceptor-doped perovskite ferroelectrics associated with ferroelectric-ferroelectric transition cycle

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Abstract – Perovskite ferroelectrics naturally exhibit multiple energetically equivalent domain states; thus, a certain domain state or a certain domain pattern is not expected to reappear once it is disturbed by a phase transition; *i.e.,* there should exist no "domain memory". This letter, however, provides direct evidence with *in situ* optical microscopy for a domain memory effect in an *aged* K^+-doped $BaTiO_3$ single crystal during a ferroelectric-ferroelectric transition cycle between tetragonal and orthorhombic phase. By contrast, the domain memory effect is absent in an unaged sample. These results suggest that the domain memory effect is associated with point defect migration during aging. Our findings can be explained by a symmetry-conforming tendency of point defects.

Ferroelectric material, known as an important class of functional material, has been found to have a variety of applications in devices [1]. Such material undergoes a transition from a paraelectric (PE) phase to a low-symmetry ferroelectric (FE) phase with a pattern of multiple domains, in which spontaneous polarization ($\mathbf{P}_S$) aligns along the same direction. As these different domain states are crystallographic symmetry-allowed and energetically equivalent, there is no preference for a particular domain state or domain pattern. As a result, once a domain pattern is reconstructed by an external electrical field or a phase transition, the original domain pattern is not expected to be recovered.

However, it is well known that the acceptor-doped perovskite ferroelectrics exhibit double polarization (P)-field (E) hysteresis loop [2–5] after aging in the unpoled state. A recent study gives evidence that this behavior corresponds to a memory process of multi-domain pattern via an intermediate single-domain state upon the cycle of fast applying and sequent removing of the electrical field [6], which also leads to a large recoverable nonlinear electrostrain [6–9]. Such a fact indicates that different domain states are not energetically equivalent after aging, and a preferable domain pattern can be developed through ferroelectric aging. The reason for such phenomenon has been ascribed to a migration of point defects in the material during aging, forming a defect distribution configuration [10–12] conforming to crystal symmetry (known as a symmetry-conforming principle of point defect [7]). The defect configuration remains unchanged during the diffusionless electrical-field cycle, and thus provides a "restoring force" [6] for such an electrical-field–activated domain memory. Although such a mechanism of aging has so far been discussed mainly for the domain memory during a fast electric-field cycle, there seems to be no reason that it is inapplicable

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to other diffusionless cyclic processes such as the quick phase transition cycle.

In this letter, we report a domain pattern memory in the aged acceptor-doped $BaTiO_3$ single crystal after experiencing a quick FE-FE transition cycle (tetragonal → orthorhombic → tetragonal, *i.e.*, $T \rightarrow O \rightarrow T$) by *in situ* optical microscopy observation. The associated *P-E* hysteresis loop measurement and its comparison with an unaged sample suggest that the domain memory during the quick thermal cycle has the same restoring force as that of the fast electrical-field cycle. Our results might provide a way to preserve the ferroelectric domain structure when experiencing a transient transforming disturbance upon temperature variation [13].

The K^+-doped (acceptor-doped) $BaTiO_3$ single crystal was used to study the domain pattern evolution during quick FE-FE transition cycle. Such single crystal was grown by the Remeika-DeVries [14,15] method with KF as flux. The as-grown $BaTiO_3$ crystal contains both K^+ and F^- impurity ions, and it was subject to an annealing treatment at 1000 °C for 10 h, which can remove the donor F^- while leaving K^+ as A-site (Ba^{2+}-site) acceptor dopant in the perovskite structure [16]. By this method we obtained the K^+-doped $BaTiO_3$ crystal, which contains oxygen vacancies due to charge neutrality requirement. The crystals were polished on top and bottom surfaces for further domain pattern observation under an optical microscope equipped with a heating and cooling stage. We used a high heating and cooling rates up to 40 °C/min, and held the sample in each target temperature for 1 min to achieve the thermal equilibrium as well as to record the domain structure by a CCD camera. Samples for electrical-property measurements were coated with silver on top and bottom sides as electrodes. Dielectric permittivity was measured by a HIOKI 3532 LCR meter with a testing frequency of 100 kHz. A workstation ferroelectric test system was used to measure the *P-E* hysteresis loop of samples with a measuring time of 50 ms.

Figure 1(a) shows the temperature dependence of dielectric permittivity for a K^+-doped $BaTiO_3$ single crystal during cooling. Two dielectric anomalies have been observed within the temperature range of −50–200 °C, suggesting two phase transitions: a PE → FE transition with T_C of 129 °C, as well as a $FE \rightarrow FE$ ($T \rightarrow O$) transition at 8 °C. The present work focuses on the domain pattern evolution during the cycle of such a $T \rightarrow O$ transition followed by its reverse transition with the temperature circulating from 30 °C to −10 °C, and then back to 30 °C. The *P-E* hysteresis loop for such a sample before aging is shown in the inset of fig. 1(a). The rectangular shape is a typical case for a ferroelectric hysteresis loop with a remnant polarization on the removing of electrical field which suggests that there is no domain memory when applying a fast electrical-field cycle.

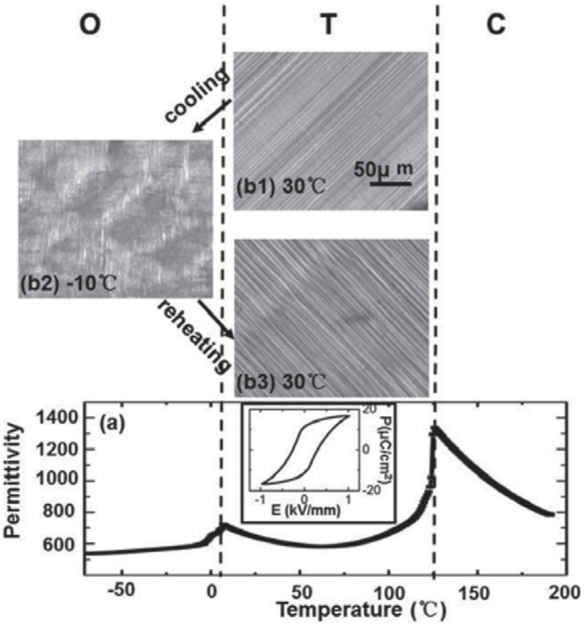

Fig. 1: (a) The change of dielectric permittivity with temperature for the K^+-doped $BaTiO_3$ single crystal showing a C (paraelectric) → T (ferroelectric) → O (ferroelectric) transition. The inset shows the *P-E* hysteresis loop for the virgin sample in the T phase. (b1)–(b3) Domain pattern evolution of the unaged virgin K^+-doped $BaTiO_3$ single crystal during the $T \rightarrow O \rightarrow T$ transition cycle. (b1) Initial T phase domain pattern (30 °C). (b2) Domain pattern when cooling to the O phase (−10 °C). (b3) domain pattern when reheating to the T phase (30 °C) which is completely different from the initial one.

Figures 1(b1)–(b3) show domain evolution during the $T \rightarrow O \rightarrow T$ transition cycle on an unaged K^+-doped $BaTiO_3$ single crystal. Initially, the sample exhibits a T phase domain structure at 30 °C (fig. 1(b1)). When cooling to −10 °C, an O phase domain pattern appears (fig. 1(b2)). If the sample is reheated to the initial temperature in the T phase (30 °C), a completely new T phase domain pattern will be established (fig. 1(b3)) compared with the initial one (fig. 1(b1)). Such a result proves the equivalence of different domain states, *i.e.,* there is no need for ferroelectric material to memorize the initial domain pattern after the phase transition cycle. This behavior is usually observed in normal ferroelectric materials.

However, here we show that after aging in the T phase (at an elevated temperature of 80 °C) for 336 h, the K^+-doped $BaTiO_3$ single crystal exhibits quite a different phenomenon. Figures 2(a)–(c) show the *in situ* microscopy observation of the domain pattern evolution of such a sample during a quick $T \rightarrow O \rightarrow T$ transition cycle. The initial T phase domain pattern of the aged sample at 30 °C has been shown in fig. 2(a). Cooling to −10 °C leads to an O phase domain pattern in microstructure (fig. 2(b)). When quickly reheating the sample to 30 °C of the T phase, unlike the undoped single crystal with energetically equivalent domain states and thus no domain memory effect, the well-aged K^+-doped $BaTiO_3$ single crystal shows an almost identical domain pattern (fig. 2(c)) with the initial T phase (fig. 2(a))

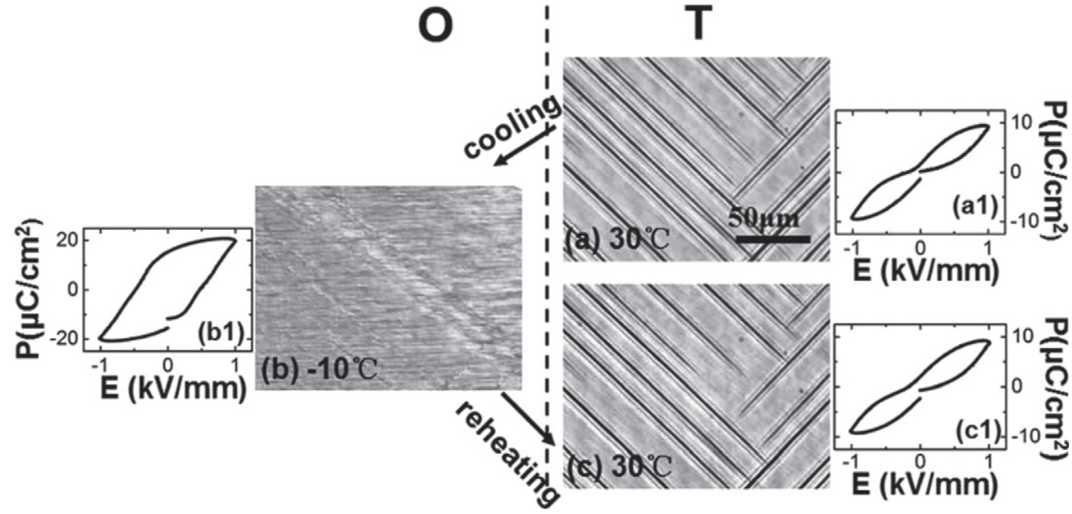

Fig. 2: Domain pattern and the *P-E* hysteresis loop evolution on the T-phase–aged K^+-doped $BaTiO_3$ single crystal during the T → O → T phase transition cycle. (a) Initial T phase domain pattern (30 °C). (b) Domain pattern when cooling to the O phase (−10 °C). (c) Domain pattern when reheating to the T phase (30 °C) showing an aging-induced domain memory during the ferroelectric-ferroelectric transition cycle. Panels (a1), (b1), (c1) are the *P-E* loop of (a), (b), (c), respectively, which show a reappearance of the double *P-E* loop after the transition cycle.

after quick transition cycling of T → O → T. The sample memorizes its initial T-phase–aged domain pattern when experiencing a quick temperature disturbance. Such a result gives direct evidence of the aging-induced domain memory effect during the quick T → O → T transition cycle. As discussed later, such a domain memory effect is a general effect in aged acceptor-doped ferroelectrics during fast transition cycles.

The *P-E* hysteresis loop evolution of the aged K^+-doped $BaTiO_3$ single crystal during the quick T → O → T transition cycle has been shown in figs. 2(a1)–(c1). Such an aged sample exhibits a double *P-E* hysteresis loop in the T phase (fig. 2(a1)), which suggests a domain memory on the fast electric-field cycle. On cooling to the O phase (−10 °C), the double *P-E* hysteresis loop has been replaced by an ordinary rectangular loop (fig. 2(b1)). However, on reheating to 30 °C of the T phase, the *P-E* loop returns to its original double shape (fig. 2(c1)), indicating that the domain memory on electrical-field cycle can still be achieved even after the transition cycle. It should be noted that such reappearance of the double loop after the transition cycle has firstly been reported in an aged ferroelectric ceramic system [17]. But direct evidence of the domain memory effect and the role of acceptor dopants have not been well recognized in that paper.

The comparison between aged (fig. 1) and unaged (fig. 2) sample shows that the domain memory during thermal cycling (fig. 2(a)) appears simultaneously with double *P-E* hysteresis loop, and disappears in the unaged virgin sample with a normal rectangular *P-E* hysteresis loop. Therefore, such a thermally activated domain memory must have the same restoring force as the domain memory during fast electrical field. The restoring force originates from a general symmetry conforming property of point defects. In addition, such consistency between temperature-activated effect and electrical-field–activated effect implicates that the domain memory effect may also exist in other aged perovskite ferroelectric materials with double *P-E* hysteresis loop [3,18,19]. Moreover, our reported domain memory on the FE-FE transition cycle, together with previously reported electrical-field–activated domain memory, suggest the generality for aging-induced domain memory effect upon the diffusionless cyclic processes.

In the following, we shall explain the origin of our reported aging-induced domain memory effect from the evolution of crystal symmetries and defect configurations/defect symmetries during the phase transition cycle. Aging manifests itself as a stabilization of domain states by the migration of point defects with time [10,20–23]. The acceptor dopant produces oxygen vacancies in the system. Such oxygen vacancies can migrate inside the system [24] and intrinsically form in the whole domain volume [18,25,26] a short-range order configuration as a result of their interaction with crystal symmetry during aging. When cooling down from the paraelectric cubic phase, the unaged acceptor-doped ferroelectric sample tends to form a cubic defect symmetry with the configuration of oxygen vacancies randomly distributed around the acceptor dopant (fig. 3(a1)). Such defect configuration does not provide any preference for the domain alignment (fig. 3(b1)), thus the unaged sample cannot achieve domain memory either in the fast electrical field or in the transition cycle as shown in fig. 1(a). Nevertheless, now the crystal symmetry is the polar tetragonal crystal symmetry, which is not compatible with this cubic

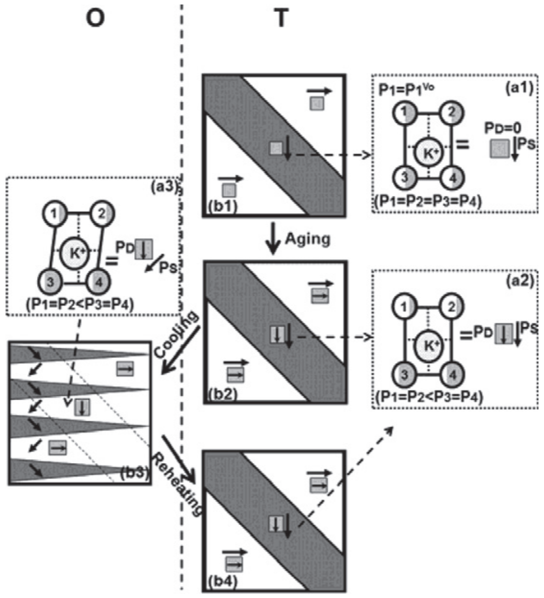

Fig. 3: Schematic illustration of the crystal symmetry and defect symmetry/defect configuration evolution during the T → O → T phase transition cycle. $\mathbf{P}_\mathrm{S}$ and $\mathbf{P}_\mathrm{D}$ are the spontaneous and defect polarization, respectively. The large and small squares or rectangles represent different crystal symmetries and defect SRO symmetries, respectively. (a1) The unaged sample shows cubic defect symmetry although crystal symmetry is already tetragonal. The oxygen vacancies randomly distributed in each site with the probability $P_1 = P_2 = P_3 = P_4$. (a2) After aging, the tetragonal defect symmetry has been developed by the migration of oxygen vacancies (with the probability $P_1 = P_2 < P_3 = P_4$), producing $\mathbf{P}_\mathrm{D}$ conforming with the $\mathbf{P}_\mathrm{S}$ direction. (a3) When cooling to the O phase, the crystal symmetry changes into orthorombic, but the defect distribution configuration remains unchanged (with the probability $P_1 = P_2 < P_3 = P_4$) due to the diffusionless origin of the T → O transition. (b1) Unaged T phase domain pattern with no $\mathbf{P}_\mathrm{D}$ (b2). After aging, each $\mathbf{P}_\mathrm{D}$ conforms with its $\mathbf{P}_\mathrm{S}$ direction in each domain. (b3) When cooling to O phase, although crystal symmetry and domain pattern change, the $\mathbf{P}_\mathrm{D}$ of each former region remains the same due to the diffusionless origin of the quick transition cycle. (b4) When reheating to the T phase, $\mathbf{P}_\mathrm{D}$ acts as a "restoring force" for $\mathbf{P}_\mathrm{S}$ to recover to its initial direction. Consequently, the domain pattern returns to the initial one.

defect symmetry. The system tends to go to the equilibrium state through the migration of oxygen vacancies during aging. In the well-aged sample, a polar tetragonal defect configuration (as shown in fig. 3(a2)) has been established conforming to the crystal symmetry, which has been evidenced by the electron paramagnetic resonance (EPR) measurement [27–29]. Such a polar defect symmetry will produce a defect dipolar moment ($\mathbf{P}_\mathrm{D}$) aligning along $\mathbf{P}_\mathrm{S}$ direction (fig. 3(a2)), and thus it will build an internal field [11,12,30,31] along $\mathbf{P}_\mathrm{S}$ to stabilize each domains state (fig. 3(b2)). When cooling to the O phase, the crystal structure as well as the relevant domain pattern has been changed (solid-line areas in fig. 3(b3)). However, the defect configuration and the associated $\mathbf{P}_\mathrm{D}$, on the other hand, remains unchanged (dashed-line areas in fig. 3(b3)) in such a diffusionless transition. The crystal symmetry as well as the defect symmetry of such a state is shown in fig. 3(a3). The point defect shows the same distribution with the same regime in the T phase (fig. 3(a2)). When quick reheating to the T phase again with only short-time stay in the O phase, the unchanged $\mathbf{P}_\mathrm{D}$ will act as a "restoring force" and thus provides a preference for each $\mathbf{P}_\mathrm{S}$ to form along its original direction. Therefore, it recovers to the initial T phase domain pattern (fig. 3(b4)). It should be noted that the field-activated domain memory has the same physics origin as the domain memory effect during the transition cycle, and thus possesses the same "restoring force". Therefore, the double *P*-*E* hysteresis loop can also be achieved in the T-phase–aged sample before and after the transition cycle shown in fig. 2(a1) and fig. 2(c1) with $\mathbf{P}_\mathrm{D}$ as the "restoring force" during the electrical-field cycle. The reappearance of the double hysteresis loop can thus be understandable.

In conclusion, this letter reports a domain structure memory effect in an aged acceptor-doped KF-flux–grown $\mathrm{BaTiO_3}$ single crystal after experiencing a quick tetragonal-orthorhombic-tetragonal ferroelectric-ferroelectric transition cycle. And it corresponds to a reappearance of the double *P*-*E* hysteresis loop during the same transition cycle in the ferroelectric property. Such a behavior can be explained by considering the point defect symmetry's tendency to conform to the crystal symmetry.

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