Aging behavior in single-domain Mn-doped BaTiO$_3$ crystals: Implication for a unified microscopic explanation of ferroelectric aging

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The change of ferroelectric, dielectric, and piezoelectric properties with time, the ferroelectric aging phenomena, has been observed in most ferroelectrics. Phenomenologically, aging can be attributed to the gradual stabilization of ferroelectric domains by defects, but the microscopic origin of the domain stabilization has remained controversial. It is unclear whether the domain stabilization is a boundary effect (caused by domain-wall-pinning) or a volume effect (stabilization of the whole domain). In the present paper, we made a *single-domain* (domain-wall-free) Mn-doped BaTiO$_3$ single crystal and studied the aging behavior of its hysteresis loop. We found that after aging, the single-domain sample shows a significant increase in the coercive field, clearly indicating a strong stabilization of the single domain. Furthermore, the sample exhibits an abnormal double hysteresis loop, which corresponds to an interesting reversible domain switching process. These are direct evidence for the stabilization of single domain by aging. Our results preclude any explanation by the domain-wall-pinning effect and strongly suggest that the volume effect is the governing mechanism for the aging in hysteresis loop. We further show that the microscopic origin of the volume effect comes naturally from a general symmetry-conforming property of point defects. Such a microscopic mechanism can explain not only the aging in hysteresis loop (large signal aging) but also the aging in dielectric and piezoelectric constants (small signal aging), thus providing a unified microscopic explanation for all kinds of ferroelectric aging.

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I. INTRODUCTION

Aging phenomena, the time-dependent changing of material properties, are well observed in almost all ferroelectrics.[1,2] It usually manifests itself in large signal properties as the appearance of a constricted or double polarization–electric field (*P-E*) hysteresis loop in unpoled samples, and in small signal properties as the decrease of the dielectric constant (at a small ac electric field) and piezoelectric constant (at small mechanical stress), etc., with time.[3–16] Ferroelectric aging cannot be understood by basic theory of ferroelectricity, as such theory does not expect any change in property with time. Furthermore, aging strongly affects the application of ferroelectrics, especially the reliability of ferroelectric and dielectric devices. Therefore, ferroelectric aging is an issue of both fundamental and practical importance, and has received much attention over the past decades.[1–16]

It is natural to speculate that ferroelectric aging is caused by a certain relaxation process, but a convincing explanation must answer two key questions: (1) Why does an "equilibrium" ferroelectric phase need to change with time? (2) What is the microscopic process of the relaxation? Historically, quite a number of models have been proposed to explain the origin of aging.[3–16] Generally, it is agreed that aging can be phenomenologically attributed to a gradual "stabilization" of domain pattern by defects (dopant, vacancy, or impurity).[4,12,13] However, a unified microscopic explanation for aging remains unclear up to now.[3,4] The central controversy is whether the domain stabilization stems from a boundary effect or a volume effect. For boundary effect, it is believed that defects migrate to the domain walls during aging and consequently pin the domain walls.[5,6] As to volume effect, it is considered that polar lattice defects align along spontaneous-polarization (P_S) orientation over the whole domain during aging and thus make domain switching difficult.[7,8] Thus, it seems that both types of models can give a self-consistent explanation for the gradual domain stabilization (or the aging effect), but the microscopic picture is completely different. In the present study, we designed a critical experiment to determine which type of mechanism plays a central role in ferroelectric aging, and also further explore the microscopic origin of the aging effect.

We notice that in the domain-wall-pinning model, the existence of domain walls is the necessary condition for aging. Thus it naturally follows that there should be no aging in domain-wall-free (*single-domain*) sample. However, in the volume effect model, aging is expected to exist even in a single-domain sample. This is a critical point to distinguish the boundary effect from the volume effect. Therefore, in the present study we made a single-domain sample and studied its aging behavior by measuring the hysteresis loop (large signal property) and simultaneously performing an *in situ* observation of domain pattern evolution during field cycling on the aged single-domain sample. This critical experiment enables us to identify unambiguously the governing mechanism for large signal aging. We further explored the microscopic origin of aging from a universal defect-symmetry principle.[9–11,17–19] As will be discussed later, the model based on this principle can also explain aging in the dielectric and piezoelectric constant (small signal properties), thus providing a unified microscopic explanation for all ferroelectric aging.
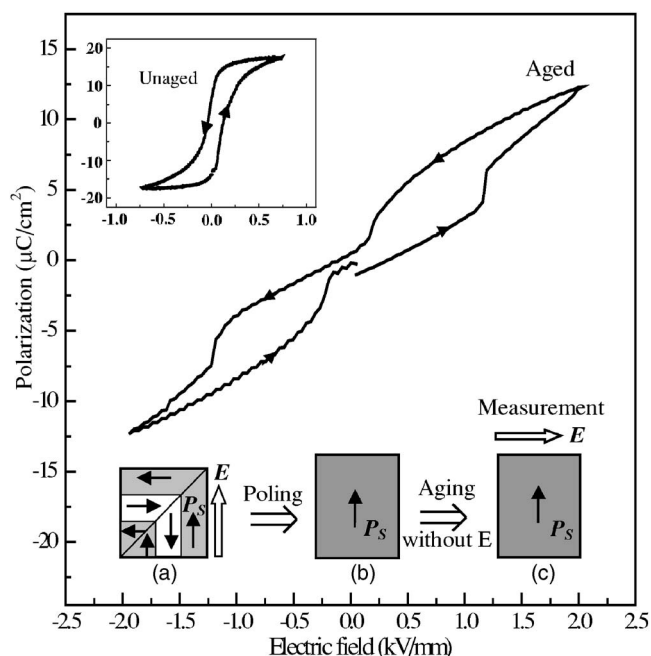
FIG. 1. A Mn-doped BaTiO$_3$ single crystal is poled with an applied electric field E along $\langle 001 \rangle$ (thickness direction) (a). As the result the sample became a *single domain* (b). Then it was aged for two weeks without E. When E is applied along $\langle 100 \rangle$ (transverse direction, perpendicular to P_S) to the aged single-domain sample (c), it shows a double hysteresis loop with a large coercive field E_C, which is contrasting with the normal hysteresis loop in the unaged state (left-top inset).

II. EXPERIMENT

The sample we used was Mn-doped BaTiO$_3$ single crystal (denoted as Mn-BaTiO$_3$). It was grown by BaCl$_2$ flux in Ar atmosphere[7] at about 1300 °C and followed by furnace cooling to room temperature. The concentration of Mn relative to the Ti site is about 0.3 mol % as determined by electron probe microanalysis (EPMA). T_C (during cooling) of this sample is about 123 °C [determined by differential scanning calorimeter (DSC)], which is slightly lower than that of pure BaTiO$_3$ crystals (about 128 °C).The Mn-BaTiO$_3$ crystal was polished to less than 100 μm thick, and then deaged (i.e., removing aging effect) by heating to above T_C and keeping for 4–5 hours. It was cooled with electric field along [001] (thickness) direction to 80 °C (this is the so-called "poling" process). After we removed the electric field, the sample became a *single domain*.The single-domain sample was kept at 80 °C for two weeks to establish a fully *aged* state. The poling and aging process is schematically shown in bottom-right inset of Fig. 1.

The aged single-domain sample was electroded by silver on two lateral sides; the electric field was thus applied in [100] (transverse) direction, which is vertical to the preceding poling direction. With such an electrode configuration, the single-domain sample undergoes a 90° switching. The hysteresis loop of such a single-domain sample was measured by a ferroelectric tester (Radiant Workstation). Then, we performed *in situ* domain observation of the same aged sample during electric field cycling by using the polarizing
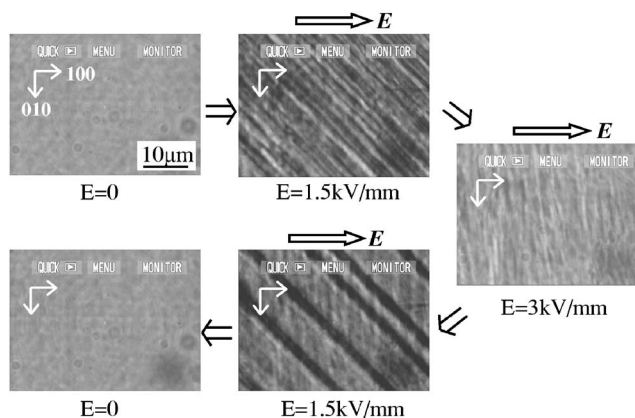

FIG. 2. Interesting reversible domain switching behavior during electric field cycling in an aged single-domain Mn-BaTiO$_3$ crystal. The crystal was poled to the single-domain state along [001] (thickness direction, along which microscopy observation was made). The typical micrographs correspond to forward electric field (along [100] direction) of $E=0$, 1.5, 3 kV/mm and reverse field $E=1.5$, 0 kV/mm, respectively. For the whole process, see video at our website (Ref. 26).

microscope in transmission mode. Detailed setup was described in our previous study.[11]

III. RESULTS

Figure 1 shows the hysteresis loop of the aged single-domain sample. It can be seen that, when the electric field is applied, the polarization increases with the electric field increasing. Interestingly, when the electric field decreases to zero, polarization does not show remanence as that of the unaged sample (shown in upper-left inset of Fig. 1) but recovers the original value. The same is true for the reverse electric field except that the polarization changes to negative. Thus, we observed a peculiar double P-E hysteresis loop in the aged single-domain sample, which is contrasting with the normal P-E hysteresis loop in the unaged state. This experiment confirmed that the hysteresis loop aging effect exists even in the single-domain sample, being the same as in the multidomain sample.[11] It is also noticed that the coercive field E_C of the aged sample (about 1.0 kV/mm) is five times larger than that of the unaged sample (about 0.2 kV/mm), which indicates that domain switching becomes very difficult after aging. The above results clearly demonstrate that even in domain-wall-free samples, there exists a strong stabilization effect that tries to stabilize the existing domain configuration.

We also did an *in situ* observation of the domain pattern evolution during field cycling for the same sample. A video for the domain switching process can be found at our website.[26] Here in Fig. 2, we show only a series of domain patterns corresponding to different electric fields. The sample was in a single-domain state before the field application [Fig. 2(a)]. When the electric field increases, some domain switching occurs; we observe a multidomain configuration [Fig. 2(b), at 1.5 kV/mm field]. With further increasing of the applied electric field, all domains are switched, and a single-

domain state is obtained [Fig. 2(c), at 3 kV/mm field]. Interestingly, when the electric field decreases, the single-domain state pattern switched back through the multidomain state [Fig. 2(d), 1.5 kV/mm field] to the original single-domain pattern [Fig. 2(e), at zero field, being the same as Fig. 2(a)]. Such a reversible domain switching during electric field cycling as observed with a microscope (domain-level) corresponds well to the macroscopic double hysteresis loop (see Fig. 1), giving direct evidence for the stabilization of the initial single-domain state after aging.

IV. DISCUSSION

A. Volume effect rather than boundary effect as the primary origin of aging

This single-domain stabilization is difficult to explain by the domain-wall-pinning effect because there are no domain walls to be pinned in single-domain sample. Furthermore, there are also two other important facts that disprove the domain-wall-pinning effect as a primary origin of aging effect. First, as shown in our recent work[11] on aging of multidomain Mn-doped BaTiO$_3$ crystals, a large field can switch all the aged multidomains into a single-domain state; yet the initial multidomain pattern is still restored from this single domain state after removing the external field. This important result cannot be explained by any domain-wall-pinning effect, because no domain walls exist in the single-domain state to be dragged back. Besides, the pinning force is known to be of very short range in nature, therefore, it is impossible to rationalize the restoration of macroscopically displaced (and ultimately eliminated) domain walls. Second, we have found that a difference exists in the "strength" of the aging effect between A-site and B-site acceptor-doped BaTiO$_3$ samples.[20] This difference in the aging effect also cannot be explained by the domain-wall-pinning effect, because both cases give rise to the same oxygen vacancy concentration, and thus it is naturally expected that the aging effect should be the same in both cases. Therefore, the so-called domain-wall-pinning effect, which is a well-known speculation, cannot be a primary reason for the aging effect.

For a single-domain sample (i.e., free of domain walls), there might be another possible cause of aging due to a different boundary effect. That is, interfaces between the sample and electrodes or surface layer of the sample may be of a different state from that of the sample interior; such interface (surface) may collect charged defects as a function of time and thus may induce aging.[4] Lambeck and Jonker[7] showed that, when a well-aged single-domain sample is etched to half its thickness (so that the charge defects are removed), it still reveals almost the same internal bias field in the hysteresis loop as that before etching. This clearly shows that the above interface (surface) effect is not the primary origin of the aging effect.

Consequently, the aging of the single-domain sample can be explained only by a "volume effect," where the stabilization of P_S or the domain is achieved by a certain distribution of defects over the whole domain volume; such a volume effect ensures the restoration of the original single-domain state during field cycling. Thus, it is clear that the volume effect rather than domain-wall-pinning effect is the governing mechanism for ferroelectric hysteresis loop aging.

In this respect, the previous volume-effect model proposed by Lambeck et al.[7,8] seems most relevant and it can overcome the difficulty of boundary effect model. Their model is based on a key assumption that defect dipoles have a tendency to follow P_S after aging, but this assumption, although reasonable, is not verified within their model. Without giving the clear microscopic picture on why defect dipoles should follow P_S and to what extent that they do follow, this model has difficulty explaining the following important facts: (1) the well-known contrasting behavior between the acceptor and donor doping effects on aging (only the former causes aging),[21] and (2) even in the acceptor-doped case, there exists a difference in the strength of aging between A-site and B-site doped BaTiO$_3$ crystals.[20] In the following, we shall explain the observed aging effect by a new microscopic volume-effect model, which is based on a general symmetry property of point defects (called "defect symmetry principle" [9–11]). Our model can provide a natural and general explanation to the observed aging effect, but also can answer the above two questions (the latter will be published elsewhere[20,21]).

B. Volume-effect model based on defect-symmetry principle and its explanation of large signal aging in a single-domain sample

The defect-symmetry principle describes a short-range-order symmetry of point defects and states that this defect symmetry will conform to crystal symmetry when in equilibrium.[9–11,17–19] Here we only give an explanation of the ferroelectric state; for details see Refs. 9–11. For Mn-BaTiO$_3$ sample (Fig. 3), it is known that the Mn dopant (with a valence of 3+ under its growth condition[22]) will occupy the Ti^{4+} site (denoted as Mn$_{Ti}$) and is charge neutralized by oxygen vacancy (denoted as V_O).[23] We define defect probability P_i^V (for a schematic two-dimensional structure, $i=1-4$) as the conditional probability of finding V_O at one of the O^{2-} sites i next to a given Mn$_{Ti}$ dopant. In a tetragonal ferroelectric structure, the neighboring O^{2-} sites are not equivalent for the Mn$_{Ti}$ dopant. It is natural that the closer oxygen site should have larger probability due to a Coulomb attractive force between an effectively negative charged dopant and a positive charged vacancy. Therefore, the defect probability should be $P_1^V > P_2^V = P_3^V > P_4^V$ when in equilibrium. This means the short-range-order distribution of defects has a tetragonal symmetry, which follows the tetragonal crystal symmetry.[9–11] The noncentric distribution of charged defects (Mn$_{Ti}$ and V_O) forms a defect polarization P_D along the direction of P_S (Fig. 3). This is the symmetry-conforming principle in the ferroelectric state case. For simplicity, the tetragonal crystal (defect) symmetry is represented by large (small) rectangle, while $P_S(P_D)$ is represented by the thick (thin) arrow.

For the ferroelectric crystal, it is well known that on cooling, a symmetry-lowering phase transition takes place at T_C. According to the basic theory of ferroelectricity, after phase transition, the system becomes a stable state; there is no rea-
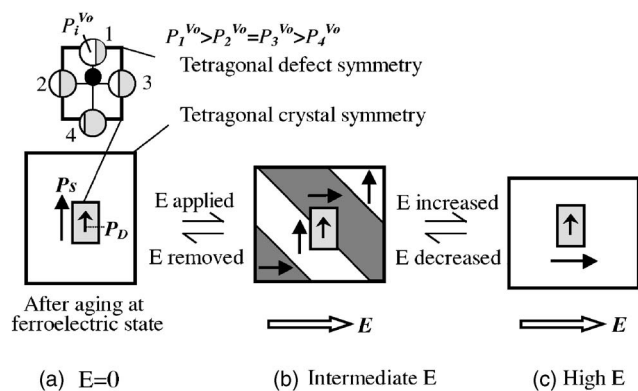
FIG. 3. Schematic explanation for defect-symmetry principle in single-domain Mn-BaTiO$_3$ crystals (a) and its explanation on aging induced reversible domain switching (a)–(c). As shown in (a), the short-range-order distribution of oxygen vacancies next to a given dopant Mn^{3+} ion shows tetragonal symmetry after aging at the ferroelectric state, conforming to tetragonal crystal symmetry. Defect (crystal) symmetry is represented by a large (small) rectangle, respectively. P_S and defect polarization P_D are represented by a thick and thin arrow, respectively. When electric field E is applied (a), P_S is switched [see the multidomain at intermediate E (b) and single domain at high E (c)], while P_D cannot be rotated and thus favored a reverse domain switching. This causes the stabilization of the original single domain (see Fig. 2), and thus generating a double hysteresis loop as shown in Fig. 1.

son to undergo any change of property with time (aging effect). However, when the system contains defects, the defect state will not be stable just after the phase transition according to the defect symmetry principle.[9–11,17–19] The reason is that in the paraelectric phase (taking BaTiO$_3$ as an example), the defect symmetry is cubic following the cubic crystal symmetry.[9–11] On cooling, crystal symmetry change abruptly at T_C to tetragonal, defect symmetry also should change to tetragonal. However, the change of defect symmetry from cubic to tetragonal requires some time to finish as it involves the short-range migration of oxygen vacancies. This is the microscopic origin of aging. Such a microscopic explanation answers the two key questions raised in the introduction: the reason for property changing with time (aging effect) is that crystal symmetry can have a sudden (diffusionless) change, while defect symmetry cannot follow immediately after the transition; as a result, the unaged ferroelectric phase is not the most stable state for point defects, so it tends to relax into a more stable state. The microscopic process of this relaxation (aging) is that the defect symmetry gradually follows crystal symmetry through the short-range migration of defects. Thus, after aging, defect symmetry conforms to crystal symmetry and P_D naturally follows P_S.

Based on this understanding, we explain the hysteresis loop aging in a single-domain sample as follows. When an electric field is applied [Fig. 3(a)], P_S will be switched to the field direction. As domain switching involves nucleation and growth, a multidomain state is observed at the intermediate field [Fig. 3(b)] before a new single-domain state (with P_S perpendicular to the initial direction) appears at a sufficiently high field [Fig. 3(c)]. Such domain switching leads to the increase of polarization. However, defect symmetry and the

associated P_D cannot change during the diffusionless domain switching process. The unchanged P_D thus favors a reverse domain switching. After removing the external field, the new single domain restores the original single-domain orientation by the force provided by P_D. As the result, the averaged polarization restores the original value. We consequently observed a double P-E hysteresis loop and a corresponding reversible domain switching in the aged single-domain sample during the electric field cycling (see hysteresis loop and domain micrographs in Figs. 1 and 2). The reason for higher E_C in the P-E hysteresis loop curve in the aged sample (see Fig. 1) is that the applied external field has to overcome an "internal field" produced by P_D before a macroscopic domain switching can happen. This makes domain switching in an aged single-domain sample more difficult compared with the unaged sample. In other words, the initial single domain is stabilized by P_D after aging. Furthermore, our mechanism can also explain a previous observation[7] that a poled (aged) single-domain sample showed a displaced hysteresis loop when measuring along P_S. According to our mechanism, the displaced loop simply comes from a reversible 180° domain switching; while in our present study, we observed a reversible 90° domain switching that gives rise to a double hysteresis loop. Both kinds of reversible domain switching are due to the domain stabilization by P_D, which comes from the defect-symmetry principle.

C. Explanation of small signal aging by defect-symmetry principle based model

Now, we have identified that the aging of the hysteresis loop is due to domain stabilization by a volume effect based on the defect-symmetry principle. As mentioned in the introduction, small signal properties also have aging effects, showing a decrease with time.[3,12–16] Then, it is natural to consider whether such small signal aging can also be explained by the same mechanism. If the mechanism can also explain the small signal aging effect, it is likely to be a unified microscopic mechanism for all ferroelectric aging. Now we discuss this possibility.

As we know, the standard definition of dielectric (ε) and piezoelectric constant (d) (in cgs units, $\varepsilon = 1 + 4\pi P/E$, $P = Zd$)[24] shows that they are proportional to the small linear polarization change (arising from ionic displacement) caused by a small electric field or mechanical stress (E or Z). It thus seems that the aging of these properties should have nothing to do with domain walls. However, many studies have shown that besides intrinsic ionic contribution, there have been considerable extrinsic contributions from domain-wall motion to ε and d.[12–16] The ε or d is the sum of these two parts (in cgs units)[25]

$$\varepsilon = \varepsilon_{in} + \epsilon_{ex} = 1 + 4\pi(\Delta P_{ion}/\Delta E + \Delta P_{dw}/\Delta E), \quad (1)$$

$$d = d_{in} + d_{ex} = \Delta P_{ion}/\Delta Z + \Delta P_{dw}/\Delta Z, \quad (2)$$

where ΔP_{ion} and ΔP_{dw} means the change of polarization induced by intrinsic ionic displacement and extrinsic domain-wall motion, respectively. In some ferroelectrics, the extrinsic domain-wall motion contributes up to 60% of the ε or

d.[16] As domain walls contribute such a significant part to the ε and d, it is generally agreed that the aging of them is due to the decrease of the domain-wall mobility (mainly the non-180° domain wall) with time.[12,13] Most of the previous work has ascribed this domain stability to a pinning effect by point defects (i.e., a boundary effect).

Now we show that the seemingly "boundary effect" in the small signal aging can have a simple volume-effect explanation, and thus makes it possible to provide a unified explanation for both large signal and small signal aging effects. As is known to all, large signal properties (hysteresis loop) correspond to a large-scale domain-wall motions (or domain switching) under an electric field, while small signal properties (ε and d) correspond to the local domain-wall motion under a small ac field. In the above-mentioned hysteresis loop aging, we had already found the increase of E_C after aging that indicates the large-scale domain-wall motion becomes difficult. This has been proved to be the result of domain stabilization by volume effect rather than boundary effect. Thus analogous to the difficulty of large-scale domain-wall motion, the local domain-wall motion can also be restricted by a volume effect and causes the decrease of small signal properties with time. Then it is possible to use our volume effect mechanism to explain such a small signal aging effect.

In Fig. 4, we schematically explain the restriction of the local 90° domain-wall motion by our mechanism. It is known that without aging, defect symmetry is cubic [represented by a small square in Fig. 4(a)]; it has no restriction to domain-wall motion. Therefore, the domain wall moves freely under a small external ac electric or mechanical field [see enlarged circle in Fig. 4(a)]. This induces a large change of polarization, ΔP_{dw}, which gives much contribution to ε and d.

However, after aging, according to the defect-symmetry principle, P_D conforms to P_S within each domain [Fig. 4(b)] and stabilizes the residing domain configuration. When an ac electric or mechanical field is applied, domain-wall motion becomes difficult, as any change of polarization near the domain-wall region encountered a resistance from the P_D which stabilized their original orientation [see enlarged circle in Fig. 4(b)]. Therefore, ΔP_{dw} becomes smaller compared with the case of an unaged sample [Fig. 4(a)]. This makes ε and d become smaller. We consequently observed that the aging induced the decrease of ε and d with time. Up to this point, we have proposed a unified microscopic explanation for both large and small signal aging: all aging stems from a gradual domain stabilization effect due to a symmetry-conforming tendency of defects.

V. CONCLUSION

In conclusion, we performed hysteresis loop measurement and *in situ* domain observation during electric field cycling
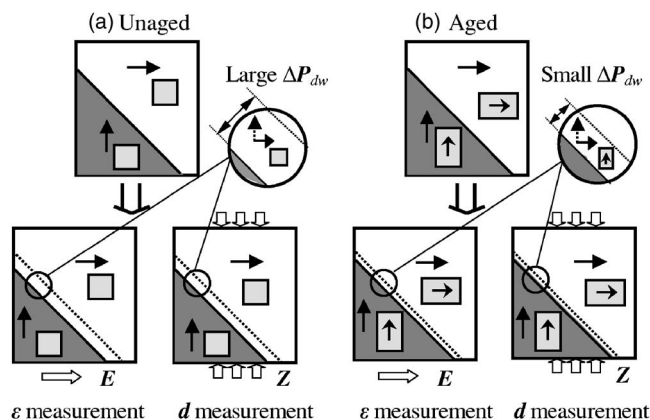

FIG. 4. Domain-wall motion under AC electric field E or mechanical stress Z (for dielectric constant ε or piezoelectric constant d measurement) for unaged (a) and aged (b) samples, respectively. This motion induces a change of polarization ΔP_{dw}, which gives extrinsic contribution to ε and d. (a) Without aging, ΔP_{dw} is larger because defect symmetry is cubic and it does not restrict domain-wall motion; thus a larger ε and d is observed. However, (b) after aging, ΔP_{dw} becomes smaller. This is because the appearance of the P_D (following P_S according to the defect-symmetry principle), which stabilizes the existing domain configuration. As a result, the domain-wall response to an external field becomes less. This explains the decrease of ε and d after aging.

for an aged single-domain Mn-doped $BaTiO_3$ single crystals. We found that a single domain crystal also has a significant aging effect. It showed a double hysteresis loop, which corresponds to a reversible 90° domain switching process. The stabilization of the single domain after aging unambiguously concludes that volume effect rather than domain-wall-pinning effect is the primary origin of large signal hysteresis loop aging. It is further shown that the microscopic origin of volume effect comes from the symmetry-conforming tendency of point defects, which stabilizes the existing domain configurations and consequently induces aging in large signal properties. Such a defect-symmetry related microscopic mechanism also naturally explains the hindrance of domain-wall motion by defect effect under weak field, thus giving a natural explanation to small signal aging of the dielectric and piezoelectric constant as well. The present study suggests that there exists a unified microscopic explanation for all ferroelectric aging.

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