External field effects on aging phenomenon of acceptor-doped BaTiO$_3$ ceramics

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Our experiments on ferroelectric aging phenomena of a series of acceptor-doped BaTiO$_3$ ceramics demonstrate that after well-aging, all samples show a similar double hysteresis loop under smaller applied electric field, regardless of ionic radius or ionic valence of the acceptor. However, with increasing the applied electric field, the completely constricted loops gradually start to open, indicating the aging effect becomes weak under larger electric field. The unified microscopic mechanism responsible for the similar aging behavior in different acceptor-doped BaTiO$_3$ ceramics may be that the larger field is considered to kinetically facilitate a part of oxygen vacancies short-range hopping. As a result, the defect dipole field provided by oxygen vacancies and the associated defect dipoles frozen in the original states decreases, thus contributing to the weaker aging effect.

I. INTRODUCTION

Ferroelectric (FE) aging effect has been observed in many oxide ferroelectrics.$^{1-4}$ This effect usually manifests itself as a spontaneous gradual change of many of their properties with time.$^5$ For example, for acceptor-doped FE systems, a long time aging in FE state will lead to the reductions of dielectric and piezoelectric parameters, an abnormal double (or constricted) ferroelectric hysteresis ($P$-$E$) loop and a large electrostrain due to the reversible domain switching, etc.$^5-10$

Previously, many mechanisms were proposed in order to explain these observed aging effects in ferroelectrics. Generally, there are three main mechanisms which are usually considered in the aging effect: (i) volume effect (formation and alignment of complex defect dipoles with respect to the direction of spontaneous polarization within FE domains in the course of time),$^5,11$ (ii) domain-wall pinning effect (migration of defects to the domain walls acting as pinning centers to lower the domain-wall energy),$^{12}$ and (iii) grain boundary effect (an intergranular second phase collecting space charges which is liquid at the sintering temperature and covers the grains as a thin layer).$^{7,13,14}$ Generally speaking, all these mechanisms are based on the stabilization of domain patterns by defects.$^2,11-13$ However, a unified microscopic explanation for all aspects of the FE aging effect is still a matter of debate.

Ren and co-workers studied the aging behavior of various FE materials, including the prominent work on a single domained (domain-wall-free) Mn-doped BaTiO$_3$ single crystal (grain boundary free),$^9$ and proposed the volume effect as the unified microscopic explanation.$^8-10$ The volume
effect refers to the formation and alignment of complex defect dipoles with respect to the direction of spontaneous polarization within the FE domains, through the migration of point defects (typically oxygen vacancies, denoted as OVs). The prominent studies of Ren group further show that the microscopic origin of the volume effect arises from a symmetry conforming short-range ordering (SC-SRO) principle, which provides the driving force for the migration of OVs.

As we all know, the relaxation of OVs is a thermally and electrically activated process, which is an important factor affecting the aging behavior. Many studies have reported the variations of $P$-$E$ loops and electrostrain with temperature and frequency. However, there is few specific report about the influence of external electric field on the aging phenomena. In this work, for the sake of the universality of physical mechanisms, we systematically investigate the effect of external electric field on aging behavior of a series of acceptor-doped BaTiO$_3$ ceramics. We will find out whether there exists a similar phenomenon and a common microscopic mechanism in all acceptor-doped BaTiO$_3$ ceramics, which do not depend on the ionic radii and ionic valences of acceptors.

II. EXPERIMENTAL DETAILS

$\text{Ba(Ti}_{0.99}\text{Mn}_{0.01})\text{O}_3$ (BT-1Mn), $\text{Ba(Ti}_{0.99}\text{Ga}_{0.01})\text{O}_3$ (BT-1Ga), $\text{Ba(Ti}_{0.99}\text{Al}_{0.003})\text{O}_3$ (BT-0.3Al), and $\text{Ba(Ti}_{0.99}\text{Mg}_{0.01})\text{O}_3$ (BT-1Mg) ceramics were chosen as our test samples, which were synthesized by the conventional solid-state reaction route. It should be noted here that the ionic radii and ionic valences of these acceptors are different from each other. The ionic radii of Mn$^{3+}$, Ga$^{3+}$, Al$^{3+}$ and Mg$^{2+}$ are 0.0645nm, 0.062nm, 0.0535nm, and 0.072nm, respectively.

For all cases, the doping level $x$ is quite low ($\leq 1.0\%$) and no structural stability of BaTiO$_3$ will be changed. According to the stoichiometric ratios, highly purified powders BaCO$_3$ (99.99%), TiO$_2$ (99.99%), Mn$_2$O$_3$ (99%), Ga$_2$O$_3$ (99.999%), Al$_2$O$_3$ (99.99%), and MgO (99.99%) were weighed, ball-mixed for 24h in alcohol, ground after drying, and then calcined at 1200$^\circ$C for 5h in air. The resultant powders were reground and further pressed under 20MPa into disks of 20mm diameter and 1.5mm thickness. The samples were sintered at 1300$^\circ$C for 6h in air. Additional grinding and sintering were performed until high quality polycrystalline ceramic samples were obtained. The structural characterizations using X-ray diffraction (XRD) with Cu K$\alpha$ radiation at room temperature were performed.

For electrical measurements, gold electrodes were sputtered on sample surfaces. Subsequently, all the samples were held at 300$^\circ$C for 4h for de-aging, followed by an air-quenching down to room temperature as un-aged (fresh) samples. To obtain the well-aged samples, the fresh samples were kept at 70$^\circ$C (slightly below the Curie point $T_C$ for the most heavily doped sample) for different times (unit in day) and then cooled down to room temperature. This is the aging process. Note that compared with the other three samples, the process of developing a well-aged state for BT-0.3Al sample is much slower. This is because the Al-doping will lead to the lattice shrinkage, with the lattice parameters and volume to be identified below. The underlying mechanism is that the Al-doping induced lattice shrinkage would kinetically hinder the OVs migration, which has been demonstrated in our previous article. The $P$-$E$ loops of all samples at room temperature were measured using the RT6000HVS standard ferroelectric testing unit.

III. RESULTS AND DISCUSSION

Before presenting the electrical data, we give the microstructure characterizations of all the as-prepared samples. As shown from the XRD patterns in Fig.1, all samples do have a single tetragonal structure at room temperature and no extra phase can be observed within the apparatus resolution. The sharp diffraction peak indicates excellent crystallinity. Table I lists the lattice parameters and volumes for all samples obtained from their x-ray data. One can see from Table I that in comparison with BT itself, no obvious change for Ga-doped (BT-1Ga) sample can be observed, noting that Ga$^{3+}$ has the similar size as Ti$^{4+}$. Nevertheless, for these large ions doped (BT-1Mn and BT-1Mg) samples, the lattice slightly expands along a and b directions, with the slight shrinkage in c direction. The increase of the volume indicates the lattice expansion for the two samples,
FIG. 1. X-ray diffraction patterns for all samples.

which is reasonable owing to the large ionic radii of Mn$^{3+}$ and Mg$^{2+}$. Moreover, the small ion Al substitution at the Ti-site results in the completely opposite changes in the lattice parameters and volume, confirming the lattice shrinkage.

Fig. 2 shows the $P$-$E$ loops for all well-aged acceptor-doped BaTiO$_3$ ceramics. We note that the similar FE aging phenomenon exists in all well-aged acceptor-doped BaTiO$_3$ samples, regardless of ionic radius or ionic valence of the acceptor. (The effects of ionic radius and ionic valence on aging phenomena have been reported in our previous article.) Fig. 2 displays that after an appropriate time of aging, all samples show a similar double hysteresis loop under smaller applied electric field, regardless of ionic radius or ionic valence of the acceptor. However, with increasing the applied field, the completely constricted loops developed under smaller electric field little by little start to open. To qualitatively describe the dependence of the aging effect on the applied electric field $E$, we denote the opening degree of hysteresis loop as $2P_r = P_r - (-P_r)$. The smaller this value is, the more obvious the aging phenomenon is. The inset of each plot in Fig. 2 shows the evaluated variation of $2P_r$ with the applied electric field $E$. Obviously, this value grows rapidly with increasing $E$ for all samples. These results allow us to conclude that for all well-aged acceptor-doped BaTiO$_3$ ceramics, the remarkable FE aging effect under smaller applied electric fields will become weaker with increasing the applied electric field.

The similarity of aging behavior in these different acceptor-doped BaTiO$_3$ ceramics suggests that there exists a unified microscopic mechanism responsible for the effect of external electric field on aging behavior. Fig. 3 schematically illustrates the details of the underlying mechanism. For all acceptor-doped samples in un-aged states, the distribution of OVs follows the cubic symmetry with randomly occupying the six equivalent sites of oxygen octahedra, while the lattice structure evolves into the polar tetragonal symmetry, generating the mismatching between the lattice symmetry and

| sample | BT   | BT-1Mn | BT-1Ga | BT-1Mg | BT-0.3Al |
|--------|------|--------|--------|--------|---------|
| $a$ (Å) | 3.9953(4) | 3.9971(3) | 3.9961(4) | 3.9988(2) | 3.9934(4) |
| $b$ (Å) | 3.9947(7) | 3.9974(1) | 3.9959(7) | 4.0045(9) | 3.9923(8) |
| $c$ (Å) | 4.0342(3) | 4.0340(5) | 4.0341(3) | 4.0331(3) | 4.0362(3) |
| $V$ (Å$^3$) | 64.385(6) | 64.456(4) | 64.416(8) | 64.567(6) | 64.337(5) |
FIG. 2. Measured hysteresis loops under different electric fields at room temperature for all well-aged samples. (a) BT-1Ga, (b) BT-1Mn, (c) BT-1Mg, and (d) BT-0.3Al. The time (day) and temperature (70°C) for the aging of each sample are labeled, respectively, in each plot. The inset of each plot shows the variation of the evaluated opening degree of hysteresis loop $2P_r$ with the applied electric field $E$.

The distribution symmetry of OVs (defect symmetry)\textsuperscript{8–10,16} The SC-SRO principle thus provides the driving force for the transformation of the defect distribution symmetry into the tetragonal one via the local migration of OVs among the six corners of oxygen octhedra.\textsuperscript{8–10,16} The long-time aging at 70°C assists kinetically in such a transformation. During the aging, the distribution symmetry of OVs tends to match with that of the lattice, and the defect electric dipoles align themselves toward to the direction of spontaneous polarization within the FE domains.\textsuperscript{16} As a result, for all acceptor-doped samples in well-aged states, the distribution symmetry of OVs is the same as that of lattice, and the defect polarization $P_D$ (black thin arrow) aligns along spontaneous polarization $P_S$ (blue thick arrow) within the FE domains (Fig.3(a)). This stable state can be schematically illustrated by Fig.3(a). It has been demonstrated that during the $P$–$E$ loop measurement, the un-switched defect symmetry and associated defect dipole generate an internal electric field $E_i$ for stabilizing the domain pattern. The microscopic defect dipole field $E_i$, calculated by the equation of $E_i = (E_1 + E_2)/2$, has been defined as a quantity describing the strength of domain stabilization.\textsuperscript{18,22} The meanings of the parameters $E_1$ and $E_2$ are described as following. When a modest electric field is applied, the FE domains will switch with $P_S$ reorientation (green thick arrow). However, these OVs and the associated point defect polarization $P_D$ remain frozen in the original states during such an abrupt (diffusionless) domain-switching process [Figs.3(a) to 3(b)].\textsuperscript{8–10} In such a diffusionless domain-switching process, this unswitched $P_D$ (black thin arrow) creates an internal field $E_1$ to resist the electric-field-induced domain switching [Figs.3(a) to 3(b)]. According to the SC-SRO principle,\textsuperscript{8–10} the state schematically illustrated by Figs.3(b) is an unstable state. Consequently, after removing the field, the unswitched $P_D$ (black thin arrow) will provide an inherent restoring force $E_2$ for switching the new domain back to its original one, where defect symmetry and lattice symmetry conform with each other [Figs.3(b) to 3(a)].\textsuperscript{23,24} This reversible domain switching mechanism explains the completely constricted hysteresis loops observed under small applied electric fields for all aged acceptor-doped BaTiO$_3$ ceramics.

The reason for the weaker aging effect under larger electric fields could be that during the larger field (large force on effectively positive-charged OVs) applying process, available energy
FIG. 3. Microscopic explanation for external field effects on aging behavior of aged acceptor-doped BaTiO$_3$ sample. Schematic graphs of the reversible domain-switching process during small electric field cycling [(a) $\rightarrow$ (b) $\rightarrow$ (a)]. Schematic graphs of the irreversible domain-switching process during large electric field cycling [(a) $\rightarrow$ (c) $\rightarrow$ (a$'$)]. Thick arrow refers to spontaneous polarization $P_S$, and thin arrow refers to defect polarization $P_D$. Solid lines represent ferroelectric domain wall, while short dashed lines represent the “domain wall” of different $P_D$ configuration. Small rectangles represent defect symmetry.

is sufficiently high for a part of OVs short-range hopping [Figs.3(a) to 3(c)]. In other words, the larger applied field may assist some OVs to migrate along electric field direction. Consequently, some associated defect polarizations $P_D$ (violet thin arrow) reorient with respect to the direction of $P_S$ (pink thick arrow) under the larger applied fields [Figs.3(a) to 3(c)].$^{7,25-27}$ As the result, the number of defect polarizations $P_D$ (black thin arrow) staying in the original states becomes fewer (Figs.3(c)), thus creates a weakening of internal electrical field $E_i$ for stabilizing the domain pattern. In this viewpoint, the internal field $E_i$ to resist the electric-field-induced domain switching decreases and thus the domain switching becomes easier and more complete, leading to a larger polarization [Figs.3(a) to 3(c)]. Furthermore, the inherent restoring force $E_2$ for switching the new domain back to its original one also weakens. Consequently, the reversal of all switched polarizations $P_S$ (pink thick arrow) could not be completed, thus giving a non-zero remanent polarization [Figs.3(c) to 3(a$'$)]. This may be the reason that the completely constricted $P$-$E$ loops gradually start to open under larger electric fields.
IV. CONCLUSION

In conclusion, we have investigated the external field effects on aging phenomena of a series of acceptor-doped BaTiO$_3$ samples. We found that after aging, regardless of ionic radius or ionic valence of the acceptor, all samples show a similar double hysteresis loop under smaller applied electric fields. However, with increasing the applied electric field, the completely constrained $P$-$E$ loops gradually start to open, indicating the aging effect becomes weaker under larger electric fields. The underlying unified mechanism responsible for the similar aging behavior in different acceptor-doped BaTiO$_3$ ceramics may be that the larger field is considered to kinetically facilitate a part of OVs short-range hopping. Thus, a smaller defect dipole field arising from defect dipoles staying in the original states is established, which contributes to the weaker aging effect.

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