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# Ferroelectric aging effect in hybrid-doped $BaTiO_3$ ceramics and the associated large recoverable electrostrain

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Acceptor doping and donor doping have been known to result in opposite ferroelectric aging effects, but the aging effect of hybrid-doped (acceptor+donor) ferroelectrics has remained unclear. In this letter the authors report the aging effect in $Mn^{3+}+Nb^{5+}$ hybrid-doped $BaTiO_3$ ceramics with acceptor fixed at 1 mol % but with donor varied from 0.5 to 2 mol %. The authors found surprisingly that ferroelectric aging existed in all the samples, no matter which of the two, acceptor or donor, was dominant: all the samples showed a double hysteresis loop after aging, but with increasing donor ($Nb^{5+}$) concentration the coercive field and hysteresis decrease. Meanwhile, a large nonlinear recoverable electrostrain up to 0.17% (due to reversible domain switching) was observed at 3 kV/mm, which exceeded that of acceptor-monodoped ceramics and was about twice the piezoelectric strain of hard lead zirconate titanate. These results demonstrate that hybrid doping is an effective way to enhance the domain-switching-related electrostrain properties. Finally, the aging effect of hybrid-doped ferroelectrics was explained. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2360933]

Aging effect, the spontaneous change of ferroelectric, dielectric, and piezoelectric properties with time, has been well observed in ferroelectrics.[1–4] As aging affects the stability and reliability of ferroelectric materials, it is usually regarded as an unwanted effect.[5] However, aging effect is not always detrimental; recent studies show that the utilization of aging effect can lead to very large recoverable electrostrain in *unpoled* acceptor-doped $BaTiO_3$ single crystals[6] and polycrystals[7,8] (such unpoled ferroelectrics normally do not show piezoelectricity), which may provide a way for electromechanical energy conversion.

Aging effect is vastly different between acceptor-doped (lower-valence doped) ferroelectrics and donor-doped (higher-valence doped) ferroelectrics. Strong aging effect is observed in acceptor-doped ferroelectrics—hysteresis loop becomes an interesting double (or constricted) loop after aging in ferroelectric state.[1–4,6–8] By contrast, such an effect does not exist in donor-doped ferroelectrics, and the hysteresis loop remains of a normal (rectangular) shape even after aging.[9] The aging effect in acceptor-doped ferroelectrics is generally considered to be due to the migration of oxygen vacancies (which is highly mobile) during aging, but the driving force for the migration has remained controversial for a long time.[1,3,10,11] Recent studies on domain switching behavior of aged multidomain[8] and single domain ferroelectrics[4] strongly indicate that the aging in acceptor-doped ferroelectrics stems from a volume effect; it originates from a general tendency of point defects (such as oxygen vacancy) to adopt a "symmetry-conforming" short-range ordered configuration;[6] such a general property of point defects was first discovered in ferroelastic/martensitic systems.[12–14] On the other hand, the absence of aging in donor-doped ferroelectric has been considered to stem from the immobility of the cation vacancies generated by donor doping, so no time-dependent relaxation can occur during aging.[5,9,15]

Here an interesting question arises: what happens in an aging effect when a ferroelectric is codoped with both acceptor and donor (i.e., hybrid doping)? Does donor doping cancel the aging effect due to acceptor doping? Multiple doping practice has been widely performed in commercial ferroelectric products to modify various properties. However, the aging effect in the hybrid-doped ferroelectrics has remained unclear. In the present letter, we report a systematic investigation on the aging effect in hybrid (acceptor $Mn^{3+}$ +donor $Nb^{5+}$)-doped $BaTiO_3$ ceramics. As will be seen in the following, we found surprisingly that no matter which of the two, acceptor or donor, is dominant, the hybrid-doped $BaTiO_3$ samples always show double hysteresis loops after aging, which normally characterizes an acceptor-monodoped system. More importantly, hybrid doping creates an important consequence on the above-mentioned electrostrain effect due to recoverable domain switching: a large nonlinear recoverable electrostrain in unpoled samples is observed, which possesses smaller coercive field and hysteresis compared with acceptor-monodoped ceramics. These results demonstrate that hybrid doping is a promising way to enhance the domain-switching-related electrostrain properties.

We prepared a series of $Mn^{3+}$ and $Nb^{5+}$ codoped $BaTiO_3$ ceramics with $Mn^{3+}$ fixed at 1 mol %, but $Nb^{5+}$ varied from 0.5% to 2%. They have a formula $Ba(Ti_{0.99-y}Mn_{0.01}Nb_y)O_3$ ($y=0.5\%$, 0.01%, 0.015%, and 0.02%), and are abbreviated as BT−1Mn−$x$Nb ($x=100y$) hereafter. This way, we obtained acceptor-dominant ($x=0.5$), equal-doping ($x=1$), and donor-dominant ($x=1.5$ and 2.0) samples. Aging was done at 60 °C($<T_c$) for 64 h to establish an equilibrium defect state. Prior to aging, all the samples were "deaged" by holding at

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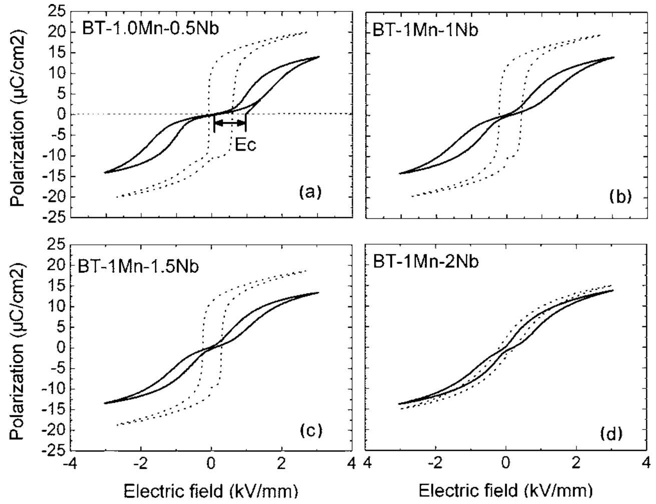

FIG. 1. Hysteresis loops before and after aging for hybrid-doped BT−1Mn−$x$Nb samples. (a) $x=0.5$, (b) $x=1$, (c) $x=1.5$, and (d) $x=2$. All the aged samples show double hysteresis loops, contrasting the normal ones (dotted lines) before aging.

300 °C for 0.5 h and were followed by a quick cooling to room temperature. The hysteresis loops and the electrostrain were measured simultaneously using the Radiant Workstation and MTI 2000 photonic sensor at room temperature. The frequency of the measurement was fixed at 10 Hz.

Figure 1 shows the experimental results of the hysteresis loop for the hybrid-doped samples with different Mn/Nb concentrations in unaged state and in aged state, respectively. All the unaged samples (just quickly cooled down to room temperature from $300\ ^\circ\mathrm{C} > T_c$) show a normal hysteresis loop, but all the aged samples show interesting double hysteresis loops. It is interesting to note that the aging effect also exists in equal-doped (1Mn–1Nb) and in donor-dominant (1Mn–1.5Nb and 1Mn–2Nb) samples, being qualitatively the same as acceptor-monodoped $(Ba_{0.95}Sr_{0.05})TiO_3-1Mn$,[6] which has a similar Curie temperature. This surprising result indicates that a donor dopant does not simply cancel out the effect of an acceptor. We shall provide an explanation later.

A quantitative analysis of Fig. 1 shows that with increasing donor ($Nb^{5+}$) concentration both coercive field [as defined in Fig. 1(a)] and the hysteresis loss (defined by the area of the loop) decrease, as can be seen in Fig. 2. This seems consistent with the well-observed "softening" effect of a donor; i.e., donor doping can make domain switching easier.[5] Therefore, our result indicates that even in the hybrid-doping situation, a donor softens ferroelectrics and makes domain switching easier.

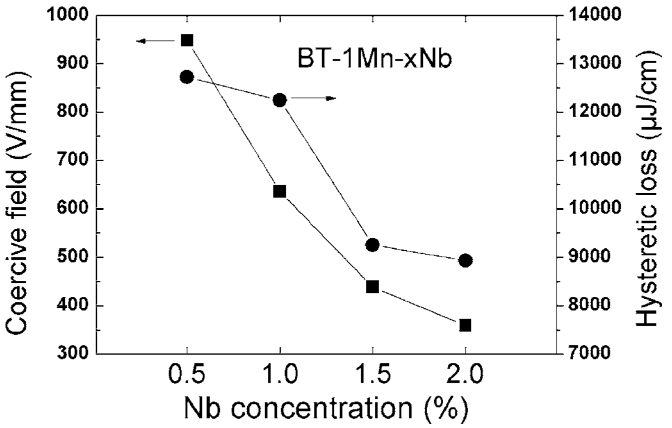

FIG. 2. Hysteretic loss and coercive field as functions of Nb concentration. The hysteretic loss and the coercive field decrease with increasing $Nb^{5+}$ doping level. The coercive field ($E_c$) for a double hysteresis loop is defined in Fig. 1(a).

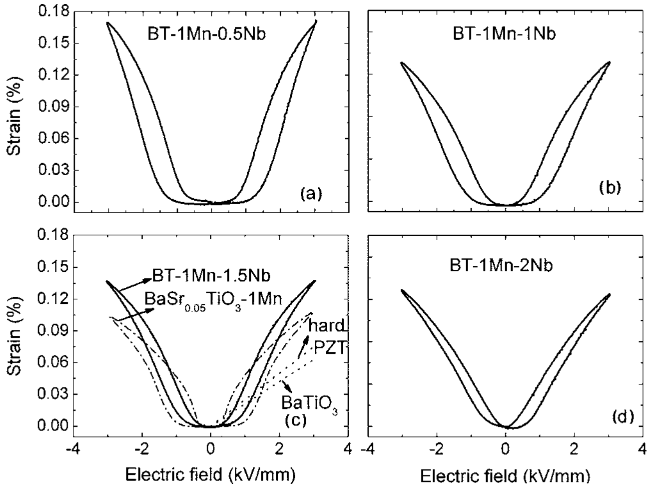

FIG. 3. Nonlinear electrostrain of aged hybrid-doped BT−1Mn−$x$Nb ceramics. (a) $x=0.5$, (b) $x=1$, (c) $x=1.5$, and (d) $x=2$. A comparison with the conventional piezoelectric effects of $BaTiO_3$ ceramics and PZT ceramics, and the electrostrain of acceptor-monodoped $(Ba_{0.95}Sr_{0.05})TiO_3-1Mn$ ceramics is made in (c).

Corresponding to the double hysteresis loops shown in Fig. 1, Fig. 3 shows interesting features in the electrostrain behavior of the unpoled hybrid-doped samples after aging. Being different from the typical irrecoverable "butterfly-shaped" strain-field curve for normal ferroelectrics, all aged hybrid-doped samples exhibited a nonlinear recoverable field versus strain curve. The maximum strain was a large value of 0.17% at 3 kV/mm for a BT–1Mn–0.5Nb sample. With increasing donor ($Nb^{5+}$) concentration the strain decreased to 0.125% for BT–1Mn–2Nb, which is still a quite large value. Furthermore, the coercive field (the critical field for domain switching) and hysteresis decreased with increasing donor ($Nb^{5+}$) concentration. Compared with linear piezoelectric effect, the electrostrain of the BT–1Mn–1.5Nb ceramics is nearly three times larger than that of $BaTiO_3$ ceramics (0.06%). Even compared with hard lead zirconate titanate (PZT) (0.075%), the electrostrain is twice as large. Compared with the similar effect reported in an acceptor-monodoped $(Ba_{0.95}Sr_{0.05})TiO_3-1Mn$, hybrid-doped BT−1Mn−$x$Nb has the advantage of having lower coercive field and loss, as shown in Fig. 3(c). It should be noted here that the electrostrain effect of our samples (without any poling treatment) is fundamentally different from the conventional converse piezoelectric effect (which requires that a sample be poled).

To understand the aging effect in hybrid-doped $BaTiO_3$, we need to first analyze its defect structure, as aging is controlled by the migration of mobile oxygen vacancies. For equal-doped BT–1Mn–1Nb, there are two possible ways for the microscopic distribution of dopant $Mn^{3+}$ and $Nb^{5+}$. The first way is that $Mn^{3+}$ and $Nb^{5+}$ form $Mn^{3+}$–$Nb^{5+}$ pairs. In such a case, the average $B$-site valence at the defect pair is 4+, which is the same as the host $B$-site ion $Ti^{4+}$. Thus charge neutrality is kept at the defect pairs, and therefore no vacancy is formed. If this were the case, we would not observe the aging effect, as no mobile defects would exist. It is

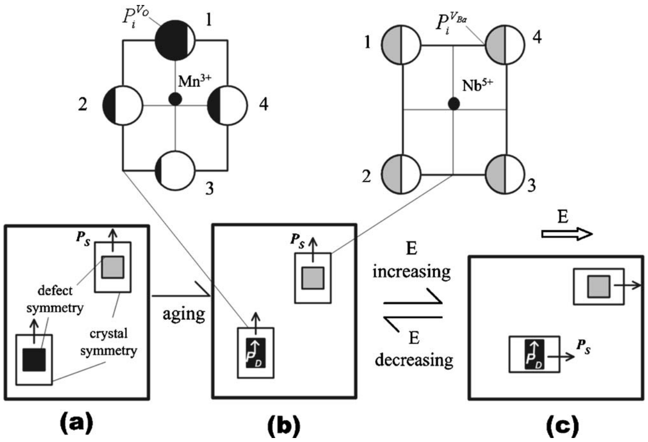

FIG. 4. Microscopic explanation for aging effect in hybrid-doped $BaTiO_3$–Mn–Nb situation. (a) Fresh ferroelectric state where the defect symmetry around an acceptor ion ($Mn^{3+}$) and that around a donor ($Nb^{5+}$) are both cubic. (b) After aging, the defect symmetry around an acceptor ion ($Mn^{3+}$) adopts a polar tetragonal symmetry (with a defect dipole $\mathbf{P}_D$), and the defect symmetry around a donor ($Nb^{5+}$) still remains cubic. $P_i^{V_O}$ is the conditional probability of finding an oxygen vacancy at site $i(i=1,2,3,4)$ around an acceptor dopant $Mn^{3+}$, and $P_i^{V_{Ba}}$ is the conditional probability of finding a cation vacancy ($Ba^{2+}$ vacancy) at site $i(i=1,2,3,4)$ around a donor dopant $Nb^{5+}$. When in equilibrium (i.e., after aging), the redistribution of oxygen vacancies makes $P_1^{V_O} > P_2^{V_O} = P_4^{V_O} > P_3^{V_O}$, while cation vacancies keep $P_1^{V_{Ba}} = P_2^{V_{Ba}} = P_3^{V_{Ba}} = P_4^{V_{Ba}}$ because of their immobility. The large rectangle represents a crystal symmetry, while the small black rectangle represents an oxygen SRO symmetry around an acceptor defect; the gray square represents the SRO of $Ba^{2+}$ vacancy around a donor defect. (c) On increasing electric field, $\mathbf{P}_S$ rotates but $\mathbf{P}_D$ keeps the original orientation; this unswitched $\mathbf{P}_D$ provides a restoring force for reverse domain switching to (b).

clearly contrary to our experimental observation. Then we consider another way of $Mn^{3+}$ and $Nb^{5+}$ distribution in the *B*-site sublattice: $Mn^{3+}$ and $Nb^{5+}$ ions are allowed to be away from each other, as their concentration is very low and thus the chance for them to form pairs is very low. By assuming such a random distribution of $Mn^{3+}$ and $Nb^{5+}$, we can see an important consequence—the formation of oxygen vacancies. In such a distribution, $Mn^{3+}$ and $Nb^{5+}$ ions are away from each other; then the perovskite unit cells centered with $Mn^{3+}$ at the *B* site become no longer charge neutral. To maintain local charge neutrality, $O^{2-}$ vacancies are formed around $Mn^{3+}$ ions. For the same reason, to keep local charge neutrality, $Ba^{2+}$ vacancies are formed around $Nb^{5+}$ ions. Therefore, when $Mn^{3+}$ and $Nb^{5+}$ ions are allowed to be away from each other, $O^{2-}$ and $Ba^{2+}$ vacancies are formed. Apparently, with increasing $Nb^{5+}$ concentration, $O^{2-}$ vacancies decrease but do not become zero. This is true even for donor-dominant compositions such as BT–1Mn–1.5Nb and BT–1Mn–2Nb. The existence of oxygen vacancies in hybrid-doped BT–1Mn–$x$Nb is the key to understanding its aging phenomenon.

Considering the mobility of oxygen vacancies and the immobility of cation vacancies at ordinary temperatures, the aging effect in hybrid-doped $BaTiO_3$ can be easily explained by a similar mechanism for acceptor-doped ferroelectrics,[7–9] as shown in Fig. 4, which is based on a universal symmetry-conforming property of point defects.[12–14] When the sample is made at elevated temperature during sintering, there is enough mobility for both oxygen and cation vacancies. Thus in the paraelectric phase, the probability of finding an $O^{2-}$ vacancy around an acceptor $Mn^{3+}$ ion and the probability of finding a $Ba^{2+}$ vacancy around a donor $Nb^{5+}$ ion will adopt a cubic symmetry, according to the symmetry-conforming property of point defects.[7–9] Immediately after the diffusionless ferroelectric transition, in the "fresh" (unaged) ferroelectric phase, the defect short-range order (SRO) symmetry remains cubic even though the crystal symmetry is polar tetragonal, as shown in Fig. 4(a). This is because a change in defect symmetry requires diffusion (thus time). However, such a state is not stable due to the mismatch between the defect symmetry and the crystal symmetry. During aging, the point defects try to relax/migrate and change the defect symmetry to become similar to the crystal symmetry. The SRO symmetry of $O^{2-}$ vacancies around an acceptor $Mn^{3+}$ ion can be gradually changed into a polar tetragonal symmetry (which produces a defect dipole $\mathbf{P}_D$) by the migration of mobile $O^{2-}$ vacancies, which is the same as the acceptor-monodoped case.[6–9] However, the SRO symmetry of $Ba^{2+}$ vacancies around a donor $Nb^{5+}$ ion still remains cubic (i.e., with no dipole moment) because the cation vacancies are immobile at such tempearture[5,9,15] [Fig. 4(b)]. When an electric field $E$ is applied on the well-aged hybrid samples, the spontaneous polarization $\mathbf{P}_S$ reorientation happens while $\mathbf{P}_D$ remains its original direction during such an abrupt (diffusionless) process [Fig. 4(b) to 4(c)]. In such a domain switching process, $\mathbf{P}_D$ acts as the resistance, and consequently it requires higher electric field to switch a domain. Macroscopically, the coercive field becomes higher compared with the fresh samples. When the electric field $E$ is removed [Fig. 4(c) to 4(b)], $\mathbf{P}_D$ acts as an inherent restoring force that switches the new domain [Fig. 4(c)] back to its original one [Fig. 4(b)], where defect symmetry and crystal symmetry conform with each other. This reversible domain switching process in aged hybrid-doped ferroelectrics explains the macroscopically observed double hysteresis loops (Fig. 1) and large nonlinear recoverable electrostrain effect (Fig. 3). With increasing donor ($Nb^{5+}$) concentration, the oxygen vacancy concentration lowers according to the above postulation on defect distribution. As a result, the strength of the defect dipole due to $O^{2-}$ vacancies and $Mn^{3+}$ ions will become weakened, and this will result in a decrease in coercive field. Therefore, although the donor dopant makes no direct contribution to recoverable domain switching, it lowers the coercive field.

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