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Abstract

Aging can significantly modify the dielectric, piezoelectric, and ferroelectric performance of ferroelectrics. However, little attention has been paid to the aging effect during ferroelectric-ferroelectric phase transitions that is essentially correlated with real applications. In this letter, the authors report the aging effect evolution between two ferroelectric phases in an acceptor-doped piezoceramics. The results show that aging-induced double hysteresis loops were exhibited in different ferroelectric phases, but disappeared during ferroelectric-ferroelectric phase transitions, suggesting the mechanism that the intrinsic restoring force for the reversible switching of domains caused by the alignment of defect dipoles was weakened due to ferroelectric dipole reorientation.

Keywords

study, ferroelectric, mechanism, during, evolution, effect, aging, transition, phase

Disciplines

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Aging effect evolution during ferroelectric-ferroelectric phase transition: A mechanism study

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Aging can significantly modify the dielectric, piezoelectric, and ferroelectric performance of ferroelectrics. However, little attention has been paid to the aging effect during ferroelectric-ferroelectric phase transitions that is essentially correlated with real applications. In this letter, the authors report the aging effect evolution between two ferroelectric phases in an acceptor-doped piezoceramics. The results show that aging-induced double hysteresis loops were exhibited in different ferroelectric phases, but disappeared during ferroelectric-ferroelectric phase transitions, suggesting the mechanism that the intrinsic restoring force for the reversible switching of domains caused by the alignment of defect dipoles was weakened due to ferroelectric dipole reorientation. © 2013 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4811168>]

The aging phenomenon, a time-dependent change in dielectric, piezoelectric, and ferroelectric properties has been observed in many ferroelectric materials. Information on the nature of the aging process can be obtained by studying the changes in the polarization – electric field (P - E) hysteresis loops which occur with aging. It is well known that after aging, a number of ferroelectric materials, such as Pb-based,¹⁻³ BaTiO₃/(Ba, Sr)TiO₃,^{4,5} KNbO₃-based,^{6,7} and Bi-based^{8,9} ferroelectrics, exhibit similar constricted P - E loops, regardless of their crystal structure and of their ionic species. The striking similarity of the aging effect in different ferroelectric perovskites was believed to originate from a general symmetry-conforming tendency of point defects, as stipulated by the symmetry-conforming short-range ordering (SC-SRO) principle.^{4,10} Such an aging effect can significantly modify the dielectric, piezoelectric, and ferroelectric performance of the materials, and plays an important role in practical applications, as in the case of aging-induced large electrostrain, which may lead to novel applications in ultra-large stroke and nonlinear actuators.⁴ Generally, most Pb-based and lead-free ferroelectric materials undergo a series of phase transitions from cubic to tetragonal (to orthorhombic) to rhombohedral with cooling from high to low temperature.¹¹ However, previous studies only focused on the aging process during a paraelectric (PE) phase (cubic) to a ferroelectric (FE) phase transition, and ignored the evolution of the aging effect during a ferroelectric-ferroelectric phase transition. If the mechanism for the aging effect is really the symmetry-conforming tendency of point defects in a ferroelectric phase, the reorientation of the dipoles during a ferroelectric-ferroelectric phase transition will cause weakening of the aging effect after the ferroelectric phase transition due to the misalignment of the defect dipoles and ferroelectric dipoles. Therefore study of the aging effect evolution during the ferroelectric phase transition is not only crucial to understand the origin of the aging effect, but also to find broad and robust potential applications of the aging effect.

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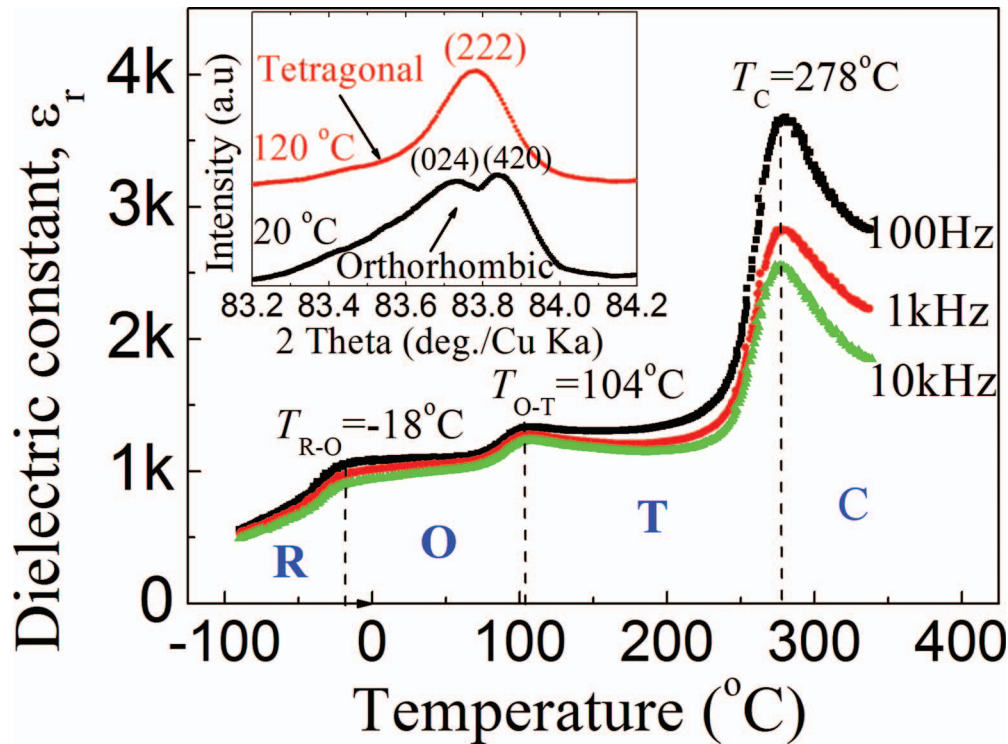


FIG. 1. Temperature dependence of dielectric constant of the $\text{K}[(\text{Nb}_{0.80}\text{Ta}_{0.20})_{0.99}\text{Mn}_{0.01}]\text{O}_{3-\delta}$ ceramic at the frequencies of 100 Hz, 1 kHz, and 10 kHz. The inset presents the XRD patterns of the orthorhombic phase at 20 °C and the tetragonal crystal structure at 120 °C. R = rhombohedral, O = orthorhombic, T = tetragonal, and C = cubic.

In this letter, we report the aging effect evolution during the transition between two ferroelectric phases, and the influence of the measurement frequency on the aging in Mn-doped lead-free $\text{K}[(\text{Nb}_{0.80}\text{Ta}_{0.20})_{0.99}\text{Mn}_{0.01}]\text{O}_{3-\delta}$ ceramic. The mechanism of the aging effect between different ferroelectric phases is well explained based on the symmetry relationship between the defect dipoles and the crystal structure.

$\text{K}[(\text{Nb}_{0.80}\text{Ta}_{0.20})_{0.99}\text{Mn}_{0.01}]\text{O}_{3-\delta}$ ceramics were synthesized using a conventional solid-state reaction technique. This compound is based on KNbO_3 , but modified by adding 20% Ta to substitute into Nb sites. 1% Mn was added as an acceptor dopant. The starting chemicals were K_2CO_3 (99.5%), Li_2CO_3 (99.9%), Nb_2O_5 (99.9%), Ta_2O_5 (99.9%), and MnO_2 (99%). Sintering was conducted at 900 °C for 2 h in a K_2O -rich atmosphere, and this was followed by sintering at 1150 °C for 0.5 h in air. Here it is noted that Mn valence state can be adjusted from 2+ to 4+ when sintered at high temperature with different O_2 partial pressure.^{12,13} Mn ions are mainly Mn^{4+} when sintered in air, and Mn^{3+} in N_2 atmosphere. In order to remove any historical effects, all the as-prepared samples were de-aged by holding them at 400 °C for 1 h, followed by an air-quench to room temperature. The quenched and de-aged samples are herein designated as “fresh samples”. Some of these un-aged samples were aged at 80 °C/120 °C and are denoted as “aged samples”. The dielectric permittivity was measured as a function of temperature using a LCR meter (HP 4192A) with a temperature chamber. The P - E hysteresis loops under various temperatures were measured in a temperature-controlled chamber using a modified Sawyer-Tower circuit.

Figure 1 shows the temperature dependence of the dielectric constant of the ceramic $\text{K}[(\text{Nb}_{0.80}\text{Ta}_{0.20})_{0.99}\text{Mn}_{0.01}]\text{O}_{3-\delta}$ at the frequencies of 0.1, 1, and 10 kHz. Three dielectric peaks are observed at about 278, 104, and -18 °C, respectively. X-ray diffraction (XRD) characterization indicates that they correspond to the phase transition temperatures of the cubic (paraelectric) – tetragonal (ferroelectric) (T_C), tetragonal (ferroelectric) – orthorhombic (ferroelectric) (T_{O-T}), and orthorhombic (ferroelectric) – rhombohedral (ferroelectric) (T_{R-O}) phase transitions,

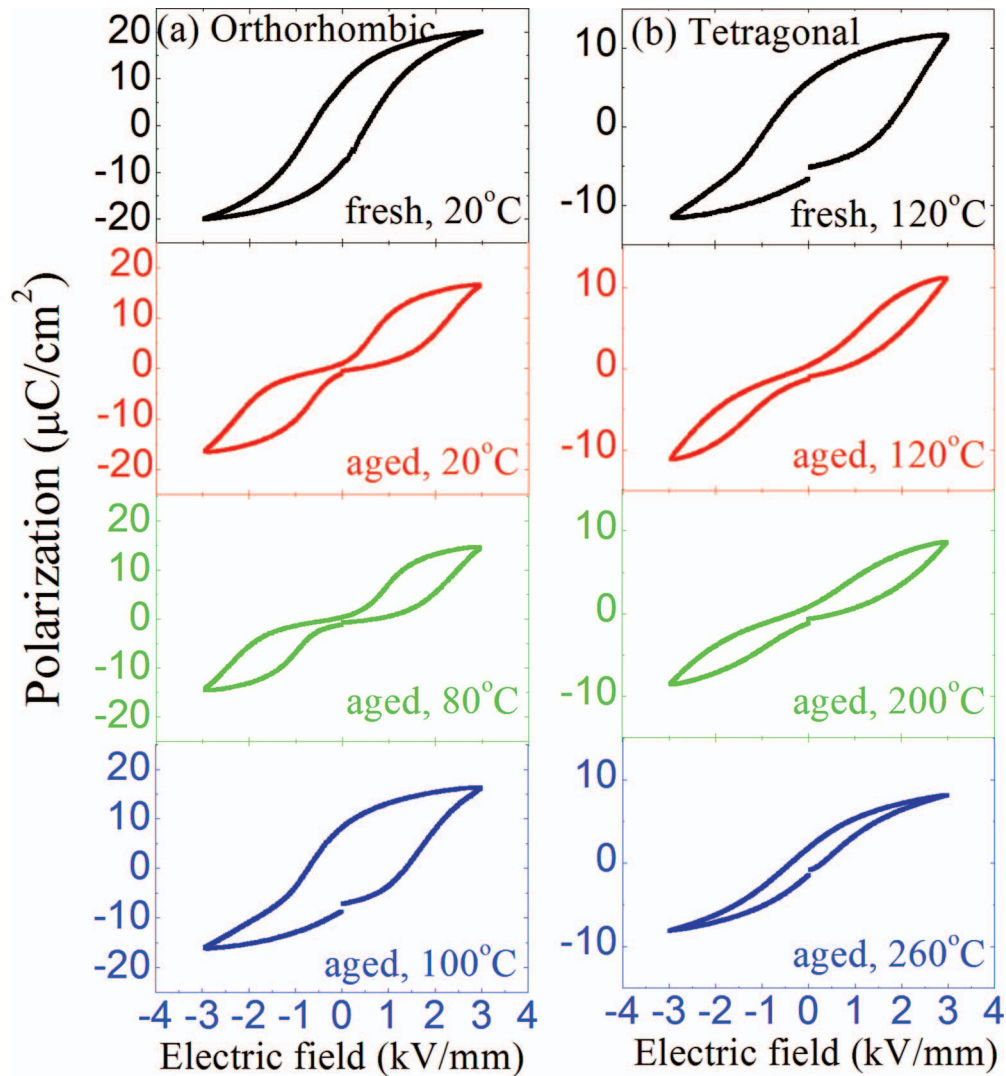


FIG. 2. P - E hysteresis loops of the un-aged (fresh) and aged $K[(\text{Nb}_{0.80}\text{Ta}_{0.20})_{0.99}\text{Mn}_{0.01}]\text{O}_{3-\delta}$ ceramic with temperature change in the orthorhombic (a) and tetragonal (b) crystal structures, respectively.

respectively. This result indicates that the sample has an orthorhombic crystal structure from -18 to 104 °C and a tetragonal crystal structure from 104 to 278 °C. Therefore, we can easily investigate the aging effect evolution between the orthorhombic and the tetragonal ferroelectric phases in the sample.

Figure 2 shows a comparison of the P - E hysteresis loops of as-sintered ceramic samples with orthorhombic and tetragonal crystal structures, respectively, measured at 5 Hz under different temperatures. For orthorhombic phase (Fig. 2(a)), in contrast with the well-known normal hysteresis loop in the fresh (un-aged) sample, after aging at 80 °C for 3 days, the sample shows an abnormal double P - E hysteresis loop, which is similar to antiferroelectric behavior. That is, as the electric field increases to the maximum, the polarization increases to the maximum. When the field drops to zero, the polarization also becomes zero. After the substitution of Mn^{4+} for the B-site ions $\text{Nb}^{5+}/\text{Ta}^{5+}$ (acceptor doping), O^{2-} oxygen vacancies (V_{O}) form to maintain charge neutrality. When fast cooled to room temperature from high temperature ($>T_{\text{C}}$), the sample becomes orthorhombic ferroelectric state from cubic paraelectric state, but the short-range order (SRO) distribution of these defects (i.e, acceptor ions and vacancies) still keeps the same cubic defect symmetry as that in the cubic paraelectric phase because the diffusionless paraelectric-ferroelectric phase transition

cannot alter the original cubic SRO symmetry of defects.¹⁴ As a result, two unmatched symmetries (i.e., the orthorhombic crystal symmetry and the cubic defect symmetry) exist simultaneously in the fresh ferroelectric state. Such a state is energetically unstable and the samples tend to a symmetry-conforming state.¹² After aging at 80 °C for 3 days in the ferroelectric state, The cubic defect symmetry changes gradually into a polar orthorhombic defect symmetry. Such a change is realized by the migration of V_O during aging, and the polar orthorhombic defect symmetry creates a defect polarization P_D (i.e, internal bias field), aligning along the spontaneous polarization (P_S) direction. When an electric field is applied to the aged orthorhombic sample, the polarization P_S is switched, but the defect polarization P_D remain in the original direction due to insufficient time for the defects to migrate, thus providing an intrinsic restoring force to cause a reversible domain switch. Consequently a macroscopic double hysteresis loop is achieved. Fig. 2(a) also shows that the constricted P - E loop will be fully opened and become normal at 100 °C near the temperature T_{O-T} (104 °C) of the orthorhombic-tetragonal phase transition. This indicates that the softening of the ferroelectric domains as the broad ferroelectric phase transition is approached leads to weakening of the pinning force of defects. Here it is noted that the double hysteresis loops will reappear when temperature is decreased to 80° from 100°, indicating the softening of the domains on approaching to the phase transition is the dominating reason for the disappearance of double hysteresis. In comparison with the orthorhombic state (Fig. 2(a)), the tetragonal fresh sample that was cooled to 120 °C from 400 °C (paraelectric state) also exhibits only a normal P - E hysteresis loop (fresh state in Fig. 2(b)). After aging at 120 °C for one day, a double P - E hysteresis loop is also observed, similar to the aging behavior in the orthorhombic state. This indicates that defect symmetry along the same tetragonal direction as the crystal symmetry has been achieved and is providing an intrinsic restoring force to cause a reversible domain switch. When the temperature increases to 260 °C, the constricted P - E loop is fully opened and become normal during the broad tetragonal (ferroelectric) – cubic (paraelectric) phase transition because the ferroelectric microdomains at high temperature weaken the pinning force of the defects.

In order to better understand the dynamics of the aging effects during the ferroelectric phase transition between orthorhombic and tetragonal phase, we observed the P - E loop evolution during temperature cycling between 80 and 120 °C, as shown in Fig. 3. The symmetries of defect dipole ($Mn'_{Nb,Ta} - V_O^{**}$) and ferroelectric dipole ($Nb^{5+}/Ta^{5+} - O^{2-}$) are also sketched in the corresponding insets. Defect dipole has defect polarization (P_D) (i.e, internal bias field) direction, and ferroelectric dipole related to the crystal structure has spontaneous polarization (P_S) direction. After aging at 80 °C for 3 days in the orthorhombic state, the normal P - E hysteresis loop becomes a double one (Fig. 3(a)) due to the defect symmetry along the orthorhombic polarization direction, which can provide an intrinsic restoring force for reversible switching of domains (Fig. 3(a) inset). When the temperature increases to 120 °C from 80 °C, the crystal structure evolves from the orthorhombic phase to the ferroelectric tetragonal phase, but the defects remain in the orthorhombic symmetry (Fig. 3(b) inset) and are thus unable to provide an effective intrinsic restoring force for the reversible switching of domains due to the lack of agreement between the defect and the crystal symmetry. Therefore, the constricted P - E loop is opened up and becomes normal (Fig. 3(b)). After aging at 120 °C for 1 day, the double P - E hysteresis loop is observed again (Fig. 3(c)), which is attributed to the defect symmetry along the tetragonal direction due to the defect (ion/vacancy) migration after aging (Fig. 3(c) inset), so that the defects consequently provide a strong intrinsic restoring force to cause reversible domain switching. When the temperature decreases to 80 °C from 120 °C, the crystal structure is transformed from the tetragonal phase to the orthorhombic phase, but the defect symmetry is still preserved in the tetragonal direction (Fig. 3(d) inset), which weakens the pinning effects of domains due to the lack of agreement between the defect and the crystal symmetry, and consequently, the constricted P - E loop becomes a normal open one again (Fig. 3(d)). After aging at 80 °C for 3 days, the defect symmetry is induced to the polarization direction (orthorhombic) again (Fig. 3(a) inset) due to the defect migration during aging, which can provide a strong intrinsic restoring force for reversible domain switching, and consequently, the double P - E hysteresis loop reappears (Fig. 3(a)). These phenomena in Figures 2 and 3 demonstrate that aging-induced double hysteresis loops can only persist in the same ferroelectric phase and will fade away during a ferroelectric-ferroelectric phase transition due to the disagreement that arises between the defect and the crystal

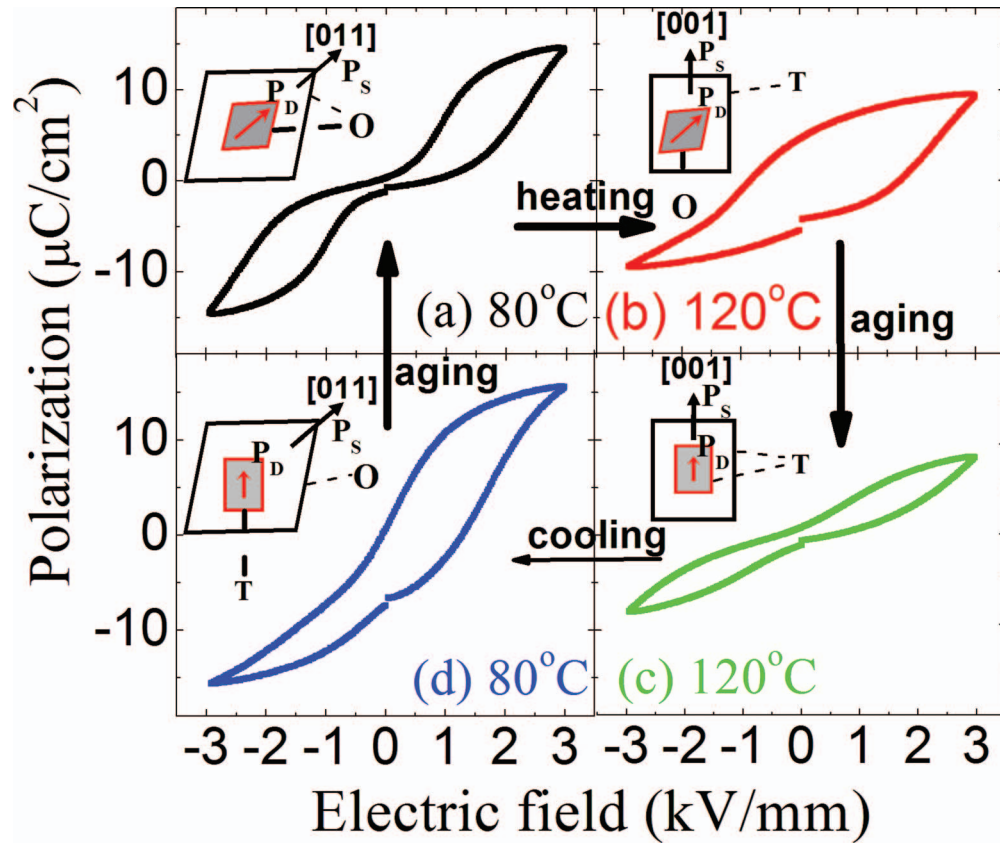


FIG. 3. Temperature-time cycle for P - E hysteresis loops of the $\text{K}[(\text{Nb}_{0.80}\text{Ta}_{0.20})_{0.99}\text{Mn}_{0.01}]\text{O}_{3-\delta}$ ceramic in the orthorhombic (80°C) and tetragonal (120°C) phases. The insets are diagrams of the corresponding defect dipole symmetry (small quadrilaterals) in relationship to the ferroelectric dipole symmetry (large quadrilaterals).

symmetry. In order to obtain effective aging evolution, the aging process should be conducted in the same crystal structure.

To investigate the time stability of defect dipoles, the P - E loops of the aged $\text{K}[(\text{Nb}_{0.80}\text{Ta}_{0.20})_{0.99}\text{Mn}_{0.01}]\text{O}_{3-\delta}$ ceramic were measured at different frequencies in the orthorhombic (20°C) and tetragonal (120°C) states, respectively, as shown in Fig. 4(a) and 4(b). It can be seen that as the frequency decreases, the P - E loops in both the orthorhombic and the tetragonal states open gradually and become normal single loops. Moreover, the double P - E loops can not be restored when the frequency is increased to the original one again. This indicates that the aging-induced double P - E loops are easily destroyed if switching takes place at a low frequency, since the defect (ion/vacancy) migration can follow the switching of the electric field if the switching time is enough long. As a result, the recovery of the switched ferroelectric domains cannot be completed due to the decrease in the intrinsic restoring force caused by the defect dipoles, resulting in a normal open P - E loop. On the other hand, it can also be seen that the constricted P - E loops become opened faster in the tetragonal phase (120°C) than in the orthorhombic (20°C), as shown in Figure 4. This should be attributed to the high migration rate of the defects at high temperature.

Here it is noted that such aging-induced double (constricted) P - E loops in ferroelectric materials appear similar to the antiferroelectric behavior in antiferroelectric materials, but they are essentially different in origin. The constricted P - E loops in the ferroelectric materials are produced by defect dipoles providing an intrinsic restoring force to cause reversible polarization switching, but such behavior will be breached under a low-frequency electric field due to the defect migration. The double P - E loops in antiferroelectric materials originate from their intrinsic structure, which comprises two sub-lattices with antiparallel spontaneous polarizations. In antiferroelectric material, a ferroelectric

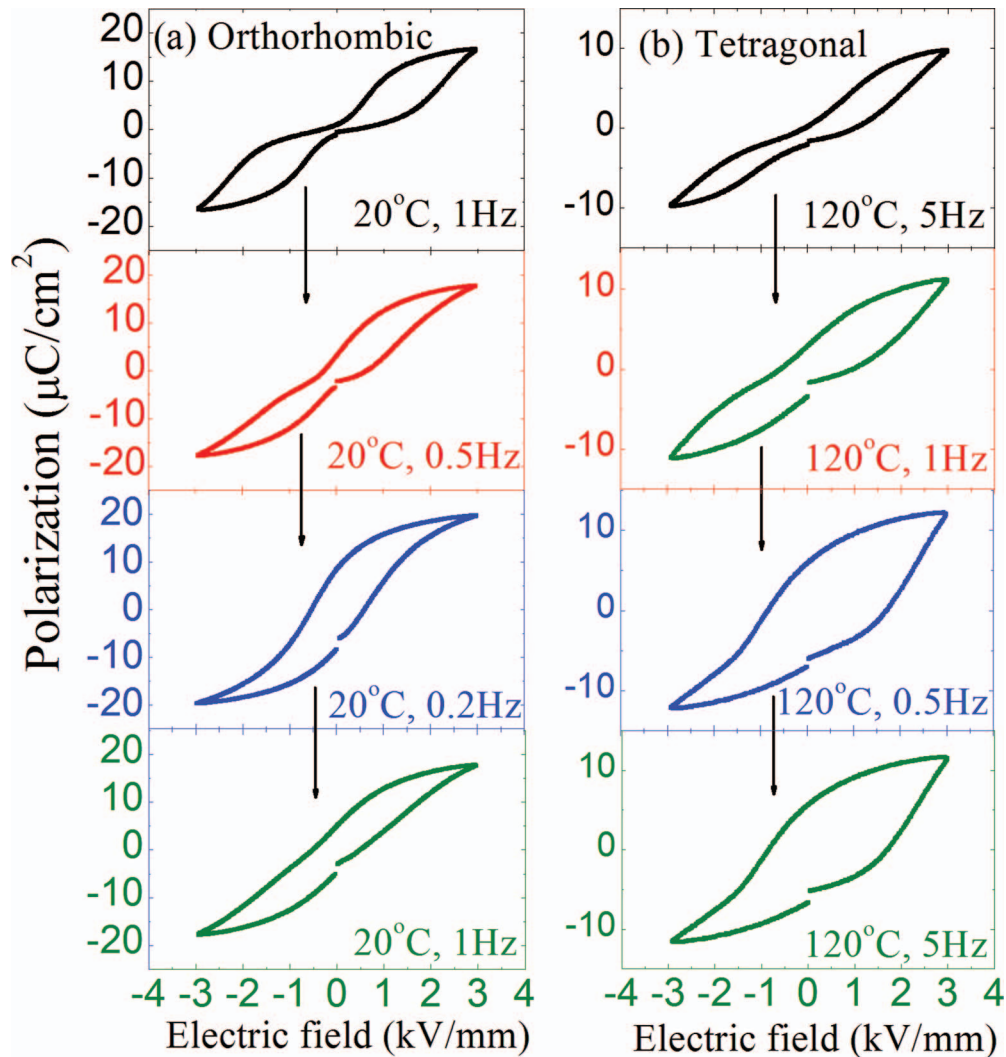


FIG. 4. P - E hysteresis loops of the aged orthorhombic and tetragonal $\text{K}[(\text{Nb}_{0.80}\text{Ta}_{0.20})_{0.99}\text{Mn}_{0.01}]\text{O}_{3-\delta}$ ceramic as the electric field is switched at different frequencies, measured at room temperature of 20°C (a) and at 120°C (b), respectively.

phase can be induced by application of an electric field, which is not related to aging or the frequency of the applied field.^{11,15} Therefore, the aging-induced double P - E loop in ferroelectric materials is only a quasi-antiferroelectric behavior.

In conclusion, we investigated the evolution of the aging effect in different ferroelectric phases after ferroelectric-ferroelectric phase transitions for an acceptor-doped $\text{K}(\text{Nb}_{0.8}\text{Ta}_{0.2})\text{O}_{3-\delta}$ ceramic sample. The results demonstrated that aging-induced double hysteresis loops can persist in the same ferroelectric phase, but disappear after ferroelectric-ferroelectric phase transition. The cause for our observation is assigned to the disagreement between the defect and the crystal symmetry, which can not provide an effective intrinsic restoring force for the reversible switching of domains. Low-frequency electric fields can also breach the stability of defect dipoles and induce de-aging behavior.

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