Aging effect and large recoverable electrostrain in Mn-doped KNbO$_3$-based ferroelectrics

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KNbO$_3$-based ferroelectrics have drawn much attention in recent years owing to their good piezoelectric performance among Pb-free piezoelectrics. However, little is known about the aging effect of these materials. In the present study, the authors systematically studied the aging effect of a Mn-doped (K$_{0.99}$Li$_{0.01}$)(Nb$_{0.65}$Ta$_{0.35}$)O$_3$ ceramic with an aim to find an aging-induced recoverable electrostrain effect based on a reversible domain switching mechanism. They found that aging in the ferroelectric state made the otherwise normal hysteresis loop into a double loop, and more interestingly the aged sample demonstrated a large recoverable electrostrain of 0.125% at 4 kV/mm in an unpoled state. Such a behavior persisted up to 140 °C and showed good recoverability. The aging-induced double hysteresis and recoverable electrostrain suggest a reversible domain switching mechanism due to a symmetry-conforming short-range ordering of point defects. The striking similarity of the aging effect between acceptor-doped $A^+B^{5+}O_3$ and acceptor-doped $A^2B^{5+}O_3$ systems indicates a common physical origin of aging. © 2007 American Institute of Physics.

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Because of the urgent demand for Pb-free piezoelectrics, KNbO$_3$-based $A^+B^{5+}O_3$ ferroelectrics with perovskite structure are drawing considerable interest for their good piezoelectric properties with high Curie temperature. However, in this class of ferroelectrics little is known about the aging effect, which is a spontaneous change of ferroelectric, dielectric, and piezoelectric properties with time. The aging effect has been commonly observed in acceptor-doped $A^2B^{5+}O_3$ ferroelectric perovskites such as Pb(Ti,Zr,O)$_3$ and BaTiO$_3$ systems. Recently, it has been used to generate a large recoverable nonlinear electrostrain in acceptor-doped BaTiO$_3$ single crystals and ceramics. In this letter we report the aging effect and the associated large electrostrain for unaged and aged (KLi$_{0.01}$)NbTa$_{0.35}$O$_3$ ceramics with an aim to find an aging-induced recoverable electrostrain effect of these materials. In the present study, the authors systematically studied the aging effect of a Mn-doped (K$_{0.99}$Li$_{0.01}$)(Nb$_{0.65}$Ta$_{0.35}$)O$_3$ ceramic with an aim to find an aging-induced recoverable electrostrain effect based on a reversible domain switching mechanism. They found that aging in the ferroelectric state made the otherwise normal hysteresis loop into a double loop, and more interestingly the aged sample demonstrated a large recoverable electrostrain of 0.125% at 4 kV/mm in an unpoled state. Such a behavior persisted up to 140 °C and showed good recoverability. The aging-induced double hysteresis and recoverable electrostrain suggest a reversible domain switching mechanism due to a symmetry-conforming short-range ordering of point defects. The striking similarity of the aging effect between acceptor-doped $A^+B^{5+}O_3$ and acceptor-doped $A^2B^{5+}O_3$ systems indicates a common physical origin of aging. © 2007 American Institute of Physics.

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FIG. 1. (Color online) Temperature dependence of dielectric constant of the (KLi$_{0.01}$)(NbTa$_{0.35}$)O$_3$–1%Mn ceramics at the frequencies of 100 Hz, 1 kHz, and 10 kHz. C=cubic, T=tetragonal, and O=orthorhombic.
an acceptor ion Mn\(^{4+}\)

try of the statistical distribution of oxygen vacancies around

in the aged sample

recoverable electrostrain of 0.125% at 4 kV/mm is achieved

ramics after aging.12,14 We further find that such aging phe-

am is the same as that for acceptor-doped A\(^{2+}\)B\(^{4+}\)O\(_3\) ferroelectrics;11–14 aging originates from the unmatching of

FIG. 2. (Color online) \(P-E\) hysteresis loop and electrostrain behavior for

as point defects responsible for the observed aging effect.

in the presence of oxygen vacancies.

alter the original cubic SRO symmetry of point defects.11 As

acceptor-doped BaTiO\(_3\)-based ceramics:11–14 aging originates from the unmatching of symmetries are not matching [see the bottom illustration of Fig. 3(a)]. According to the SC-SRO principle,16,17 such a state is energetically unstable. Therefore, after aging for a long time in the ferroelectric state, defect symmetry gradually changes into a polar tetragonal one, following the polar tetragonal crystal symmetry, as shown in Fig. 3(b). Such a change into polar defect symmetry is realized by the migration of oxygen vacancies during aging, and the polar tetragonal defect symmetry creates a defect polarization \(P_D\), aligning along the spontaneous polarization \(P_S\) direction [Fig. 3(b)]. When an electric field is applied to the aged tetragonal \((KLi_{0.01})_{0.128}$ $\times (NbTa_{0.35})_{0.1} - 1$ Mn sample, \(P_S\) is switched to the field \(E\) direction, but the defect symmetry and associated \(P_D\) cannot have a sudden change, as shown in the bottom illustration of Fig. 3(b). Therefore, after removing the electric field, the unchanged defect symmetry and the associated \(P_S\) cause a reversible domain switching, and consequently a macroscopic double-hysteresis loop and a large recoverable electrostrain behavior, as observed in Fig. 2. Clearly, the explanation is the same as that for acceptor-doped \(A^{2+}\)B\(^{4+}\)O\(_3\) ferroelectrics;11–14 aging originates from the unmatching of the defect symmetry with the crystal symmetry after a structural transition; it is not sensitive to the structure details such as the valence of the constituent ions. This explains why the aging effect seems insensitive to the valence of the constituent ions in the perovskite structure.

The variation of \(P-E\) hysteresis loop and electrostrain of the aged sample with temperature is shown in Fig. 4(a). The temperature dependence of the saturation polarization and recoverable electrostrain is presented in Fig. 4(b). It can be seen that the aging-induced double-hysteresis loop and recoverable electrostrain behavior can persist up to 140 °C, which indicates a wide temperature range for this effect. However, the maximum polarization and strain gradually decrease with increasing temperature with a gradual drop in recoverability. When the temperature exceeds 140 °C, the hysteresis loop becomes a normal one and the strain becomes very small. This may arise from two factors. Firstly, vacancy migration may become so fast at such a temperature that \(P_P\) can follow the change of the electric field direction \(E\). Then \(P_D\) cannot cre-
FIG. 4. (Color online) (a) Temperature dependence of $P$-$E$ hysteresis loop and electrostrain of the aged (KLi$_{0.01}$)(NbTa$_{0.35}$)O$_3$–1Mn ceramics. (b) Temperature dependence of maximum polarization and strain of the aged sample at 4 kV/mm.

We further investigated the stability of the recoverable electrostrain of the aged sample against field cycling. The result is shown in Fig. 5. It shows that the electrostrain has a good recoverability even after 10 000 cycles at 4 kV/mm. Interestingly, the maximum strain increases slightly with increasing number of cycles. This may be due to the migration of a small portion of point defects during the cycling process, which results in a weakening of the defect dipole $P_d$. As the result, the resistance against domain switching decreases, and hence domain switching becomes easier and more complete. This contributes to a larger strain level.

The above results about the aging effect in Mn-doped KNbO$_3$-based ferroelectrics are very similar to those in acceptor-doped BaTiO$_3$ materials. The striking similarity in aging behavior between acceptor-doped $A^+$B$^5$O$_3$ and acceptor-doped $A^+$B$^4$O$_3$ system can be explained by a common mechanism of aging: the symmetry-conforming short-range ordering of point defects. As discussed above, such mechanism relies essentially on symmetry, not on the details of the ionic species. The key idea is that point defects tend to adopt a statistical symmetry that follows the crystal symmetry. This tendency does not depend on the crystal structure or the nature of ions. 

In conclusion, we found an interesting aging phenomenon, the double-hysteresis loop and recoverable electrostrain behavior, in an acceptor-doped $A^+$B$^5$O$_3$ perovskite system: the tetragonal (KLi$_{0.01}$)(NbTa$_{0.35}$)O$_3$–1Mn. The aged sample possesses a large recoverable nonlinear electrostrain of 0.125% at 4 kV/mm. Such effect persists over a temperature range from 20 to 140 °C and shows good stability against field cycling. The aging effect of this $A^+$B$^5$O$_3$ compound shows a striking similarity to that of $A^+$B$^4$O$_3$ based systems. This similarity suggests a common physical origin of aging. Aging-induced nonlinear electrostrain effect may provide an alternative way to enhance the electromechanical coupling in Pb-free ferroelectric systems. Finally, we note that a slightly pinched hysteresis loop has been reported in a nominally undoped KNbO$_3$-based ferroelectric after thermal cycling. Although no explanation was given, it might bear some relation with the effect we reported here.

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References:

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