AIP | Applied Physics Letters

Aging associated domain evolution in the orthorhombic phase of 001 textured (K0.5Na0.5)Nb0.97Sb0.03O3 ceramics

Jianjun Yao, Jiefang Li, D. Viehland, Yunfei Chang, and Gary L. Messing

Citation: Applied Physics Letters **100**, 132902 (2012); doi: 10.1063/1.3698154
View online: http://dx.doi.org/10.1063/1.3698154
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/100/13?ver=pdfcov
Published by the AIP Publishing

Aging associated domain evolution in the orthorhombic phase of ⟨001⟩ textured $(K_{0.5}Na_{0.5})Nb_{0.97}Sb_{0.03}O_3$ ceramics

Jianjun Yao,[1,a)] Jiefang Li,[1] D. Viehland,[1] Yunfei Chang,[2] and Gary L. Messing[2]
[1]*Department of Materials Science and Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, USA*
[2]*Department of Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania 16802, USA*

(Received 20 December 2011; accepted 10 March 2012; published online 26 March 2012)

Aging effect due to domain evolution in $(K_{0.5},Na_{0.5})Nb_{0.97}Sb_{0.03}O_3$ ⟨001⟩ textured ceramics was investigated by piezoresponse force microscopy. We find that aging effect is pronounced in the orthorhombic single phase field. A more uniform and finer domain structure on the order of several hundred nanometers was observed after aging and is believed to originate from defect-migration. After poling, large domains (∼10 μm) with smooth boundaries were found in the aged condition due to the more readily redistribution of uniform and finer domain structures after aging. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3698154]

In the past decade, environment concerns have inspired research on high-performance lead-free piezoelectrics, which have the potential to replace lead zirconate titanate (or PZT) solid solutions. Since 2004 when Saito *et al.* proposed the $(K_{0.5}Na_{0.5})NbO_3$ (or KNN) family as lead-free piezoelectric alternative,[1] much work has been performed to further improve its piezoelectric properties: through compositional modifications and shifting the polymorphic phase boundary (PPB).[2] A significant increase of the piezoelectric coefficients in ⟨001⟩ textured KNN ceramics compared to randomly oriented ceramics is due to an enhanced ordering of the distribution of grain orientations along ⟨001⟩. It is known that ferroelectrics with engineered domain configurations exhibit significantly improved piezoelectric responses along nonpolar axes.[3,4] The ⟨001⟩ texture guarantees that the application of E is along [001], which is a different crystallographic orientation than the {110} polarization vector in the orthorhombic phase of KNN.

KNN undergoes a structural phase transformation sequence on cooling of paraelectric cubic (C) $\xrightarrow{\sim 400\,^{\circ}\mathrm{C}}$ ferroelectric tetragonal (T) $\xrightarrow{\sim 210\,^{\circ}\mathrm{C}}$ ferroelectric orthorhombic (O).[5] The $T \rightarrow O$ boundary is known as the PPB, designating its difference from the morphotropic phase boundary (MPB) of Pb-based systems. The PPB of $K_xNa_{1-x}NbO_3$ solid solutions is nearly independent of x, remaining almost independent of temperature for $0 < x < 1$. One of the major differences between PPB and MPB-based ferroelectrics lies in the temperature dependence of the piezoelectric properties. The PPB-based ones generally exhibit large changes in the piezoelectric coefficient near the PPB; however, the MPB systems are only weakly temperature dependent and thus offer a broad temperature range for usage. The observed enhancement of the piezoelectric coefficient in KNN was first attributed to an MPB between orthorhombic and tetragonal phases.[6–8] However, later studies reported a not strong temperature dependence of the electromechanical properties and the existence of a O → T PPB near room temperature.[9] Recently, x-ray studies of textured KNN ceramics have shown phase coexistence near the PPB over a 30 °C temperature range, where the relative phase volume fractions change. Furthermore, increasing E applied along the [001] resulted in a notable increase in the volume fraction of the T phase, effectively shifting the O → T boundary to lower temperatures. The piezoelectric properties increased with T volume fraction.[10]

The structure of KNN has been reported to be dependent on stoichiometry. At room temperature, the orthorhombic phase is not the only structure that has been reported. A monoclinic structure has also been found for compositions near the boundary at $x = 0.5$.[11] Small substituent concentrations are known to result in the coexistence of orthorhombic and tetragonal phases.[12,13] However, for ⟨001⟩ textured $(K_{0.5}Na_{0.5})Nb_{0.97}Sb_{0.03}O_3$ (KNN-3%Sb) ceramics, x-ray investigations show a single orthorhombic phase field.[14] It has been suggested that nanodomains play a vital role in the high piezoelectric property near the MPB of Pb-based perovskites.[15] Prior studies of domain structures in KNN have revealed that the domain widths are on the order of 20–50 nm. It was found that orthorhombic and tetragonal domain structures coexisted, with domain walls intersecting between nano-domains at 90° which existed adjacent to submicron domains having 45° intersections.[13,16] The submicron domains were assembled of tetragonal nanodomains having the same (110) twin walls. More recently, it was shown that KNN has various domain morphologies, including featureless domains and striplike domains.[17,18]

The KNN system is known to have a unique aging effect, which has been utilized to improve its piezoelectric properties.[12] A defect migration model has been proposed to explain the origin of aging.[12,19,20] This model was based on x-ray diffraction data of KNN ceramics, which underwent different thermal treatments. In addition, an aging and re-poling induced enhancement of the piezoelectric properties has been reported for KNN compositions with coexisting orthorhombic (O) and tetragonal (T) phases.[12] However, micro-structural studies concerning domain evolution associated with aging and re-poling have not yet been reported.

a)Electronic mail: jjyao@vt.edu.

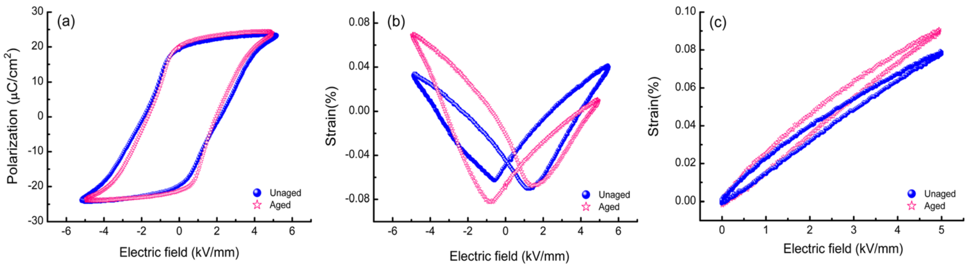

FIG. 1. Dynamical electromechanical responses for unaged and aged KNN-3%Sb textured ceramics. (a) Polarization hysteresis loops, (b) bipolar strain hysteresis curves, and (c) unipolar strain hysteresis loops.

Aging has been proven to be effective in enhancing field induced domain switching in single T phase $BaTiO_3$ crystals,[19,20] via a defect symmetry conforming principle. A symmetry-conforming property could provide a restoring force for reversible domain switching and consequently a large recoverable electro-strain.[19]

Here, we present a study of domain evolution driven by aging of ⟨001⟩ textured $(K_{0.5}Na_{0.5})Nb_{0.97}Sb_{0.03}O_3$ (KNN-3%Sb) ceramics in the orthorhombic single phase field. Aging and re-poling increased the piezoelectric properties, as previously reported.[12] We find that aging results in a more uniform and finer domain structure, which is pronounced for KNN-3%Sb. Large domains with smooth boundaries were observed in this aged sample after poling.

The ⟨001⟩ textured KNN-3%Sb ceramics were prepared by a templated grain growth (TGG) technique developed by Chang *et al.* with strong pseudocubic ⟨001⟩ orientation ($F_{001} = 97\%$).[14] Wafers of ceramics were cut into dimensions of $3 \times 3 \times 0.3\,mm^3$ and were subsequently electroded on both surfaces with gold. The samples were poled in silicone oil at room temperature under a dc field of E = 3 kV/mm for 20 min, and the aging process was carried out at 170 °C for 30 days. The following property studies were then performed. Polarization hysteresis (P-E) and strain vs E-field (ε-E) curves were measured at a frequency of 1 Hz using a modified Sawyer-Tower circuit and a linear variable differential transducer (LVDT) driven by a lock-in amplifier (Stanford Research, SR850). Careful investigations of the domain structure were performed by piezoresponse force microscopy (PFM) (DI 3100 a, Veeco). For the PFM studies, gold electrodes were deposited on the bottom face of the samples by sputtering, the electroded face was then glued to the sample stage, and the opposite unelectroded surface was scanned by the SPM tip (Veeco, DDESP-10). An ac modulation voltage of 4 V (peak to peak) with a frequency of 22 kHz was applied between the conductive tip and the bottom gold electrode. TEM work was carried out on a FEI TITAN 300 electron microscopy operating at 300 kV, with a double-tilt sample holder.

The P-E hysteresis loops of unaged and aged KNN-3%Sb ceramics are shown in Fig. 1(a). A remnant polarization of $P_r = 20.5\,\mu C/cm^2$ and a coercive field of $E_c = 2.1$ kV/mm were found in the unaged condition. Aging makes only a slight difference in these values with $P_r = 21.5\,\mu C/cm^2$ and $E_c = 1.9$ kV/mm. The bipolar ε-E curves for the unaged and aged conditions are shown in Fig. 1(b). Aging results in a significant increase of the induced strain: from 0.1% for the unaged condition to 0.16% for the aged one. However, the unipolar ε-E curves revealed a less pronounced increase, as in Fig. 1(c): from 0.079% (unaged) to 0.090% (aged). The reduced strain of the unipolar ε-E response is consistent with changes in the induced polarization, via electrostriction (Q), as

$$\frac{\varepsilon_{unaged}}{\varepsilon_{aged}} = 0.88 \approx \frac{Q}{Q}\frac{P^2_{unaged}}{P^2_{aged}} = 0.91.$$

Thus, the changes in the unipolar strain with aging arise due to those in polarization. However, the much larger changes in the strain of the bipolar ε-E curves with aging must result from domain switching contributions, potentially similar to that of the T domains in the $BaTiO_3$ crystals by the symmetry conforming concept.[19] This would imply significant changes in the domain distribution with aging and/or subsequent poling.

Representative PFM images of the domain morphology for ⟨001⟩ textured KNN-3%Sb with different heat treatments are shown in Fig. 2. In the as-received (unaged) condition (Figs. 2(a) and 2(b)), the domain morphology did not possess a preferred crystallographic orientation, but rather had irregularly shaped boundaries. The size of these domains varied over a wide range between 0.1 and 5 μm. This abnormal domain distribution may result from residual stresses remaining within the grain structure after sintering. Such domain distributions and morphologies may not be beneficial for enhanced properties, as previous studies near a MPB have shown that the piezoelectric properties significantly increase with decreasing domain size.[13,21–27] The reduced domain

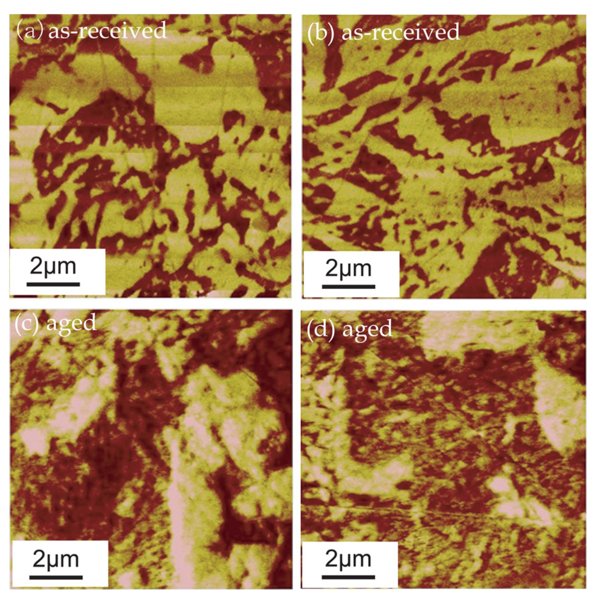

FIG. 2. Domain morphologies of KNN-3%Sb textured ceramics in two different conditions: (a), (b) as-received; (c), (d) aged.

size near the boundary is a result of a low anisotropy, allowing for low symmetry structurally bridging phases. A reduced domain size may enable domain redistribution under application of electric field E.

Representative domain morphologies of the aged condition at 170 °C are shown in Figs. 2(c) and 2(d). Compared with the as-received (unaged) state, a clear difference can be seen. First, many small domains emerged after aging whose size was on the order of several hundred nanometers. Second, the domain distribution was more uniform, and no notable domain boundaries were found probably due to the small size. These changes are believed to be due to defect migration.[12,19,20] Note that aging took place at 170 °C, which is in the T phase field and above the O → T boundary near 130 °C. Thus, following a symmetry conforming principle, mobile defects would redistribute with time under field developing a tetragonal-like conforming symmetry. Under bipolar drive at temperatures below the PPB, this frozen-in symmetry conforming condition could then enable domain switching between {110} orthorhombic variants via the structurally bridged tetragonal conforming state.

We studied the effect of poling before and after aging, as shown in Fig. 3. Our findings support the above arguments that enhanced bipolar strain results from domain contributions via defect symmetry conformation. In the as-received (unaged) condition, poling resulted in irregular domain patterns of 2–5 μm in size that had rough boundaries (see Figs. 3(a) and 3(b)). When the aged condition was subsequently poled, the domain morphology had notably different features (Figs. 3(c) and 3(d)): macro-domains of 10 μm in size became apparent with smooth boundaries. Note that a single domain state was not observed. The more uniform and finer domain structure in the aged condition (Figs. 2(c) and 2(d)) is more readily to be redistributed under E, evolving into larger macro-domain plates. Subsequent application of E along a nonpolar axis at room temperature may then result in broadened domain walls via the frozen-in defect symmetry conformation along {001}. Such broadened domain walls could serve as nuclei for domain switching.[28] We note that the domain patterns of ⟨001⟩ textured KNN-3%Sb ceramics observed here did not have any preferred orientations and that different domain morphologies of KNN ceramics have been reported.[16–18,29] We believe that such differences may result from inhomogenous phase structures due to stoichiometry or sintering conditions.

We also investigated the domain and local structures in the aged condition by transmission electron microscopy (TEM). Typical domain structures by bright field and lattice imaging are shown in Fig. 4. The bright field image revealed the presence of fine domains of 30–500 nm lengths and 10–30 nm widths. It is noted that comprehensive investigations were carried out on ~10 regions and irregular domain structures are the typical domains based on numerous observations (~30 images). Also, the domain pattern observed by TEM is consistent with that by PFM in the aged condition. Note that the domain size observed by TEM is often smaller than that by PFM, which is believed to originate from a decreasing domain size with sample thickness. A selected area electron diffraction (SAED) pattern is shown in the inset of Fig. 4(a). This inset did not reveal diffuse scattering along ⟨001⟩ or super-reflections, as recently reported.[17,29] The super-reflections observed in A-site perovskites were believed to originate from the possible octahedral tilting or A-site cation ordering.[30,31] To investigate the possible existence of localized ordering of A-site cations or octahedral tilting on the nanoscale, high resolution lattice images were obtained for the aged condition (Fig. 4(b)). No local structural modulation was observed in the lattice image and also the power spectrum of the lattice image (shown as inset of Fig. 4(b)) was consistent with that of the SAED, which demonstrates that A-site cation ordering or octahedral tilting does not exist on the nanoscale for the KNN-3%Sb textured ceramics.

Our findings indicate that the defect symmetry conforming principle can have important consequence on systems containing a PPB boundary between O and T phases. This boundary is driven by temperature rather than by composition as seen for the MPB.[32] Thus, electric fields applied in the high temperature phase develop a defect conforming symmetry consistent with the high temperature phase. On cooling through the PPB, the defect-conforming symmetry of the high temperature phase is then preserved into the

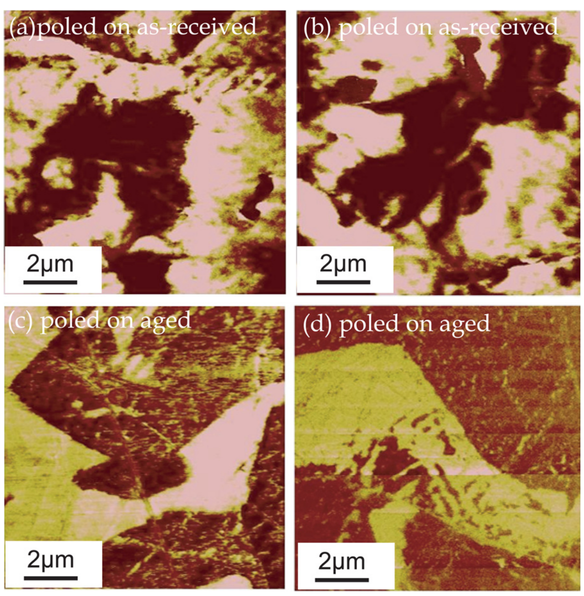

FIG. 3. Domain morphologies of poled KNN-3%Sb textured ceramics with E = 3 kV/mm in two different conditions: (a), (b) poled on as-received; (c), (d) poled on aged.

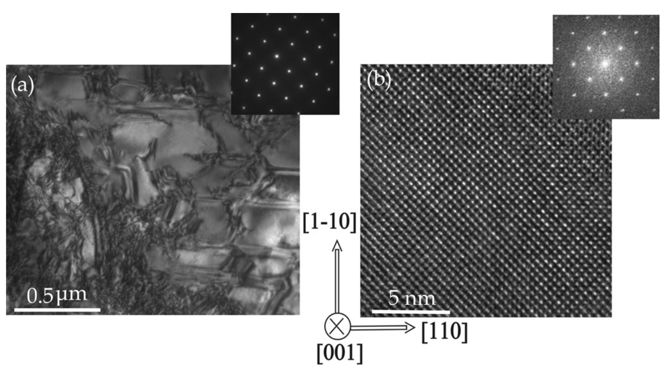

FIG. 4. TEM results for KNN-3%Sb textured ceramics: (a) Bright-field image along the [001] zone axis, where the inset shows a SAED; (b) ⟨001⟩ lattice image, where the inset is the corresponding power spectrum.

lower temperature one. This provides, in a sense, the low temperature phase with a structural link to the high temperature one. Such a link could have significant consequences for domain switching, where fields applied along crystallographic directions different than that of the polarization vector could result in enhanced bipolar strains.

In summary, aging associated domain evolution in KNN-3%Sb textured ceramics has been observed. The results reveal that there is a pronounced aging effect is in the orthorhombic single phase field. More uniform and finer domain structures were observed, which are believed to originate from defect-migration. Large sized domains ($\sim$10 μm) with smooth boundaries were found in the aged condition after poling. Both TEM and HRTEM studies did not reveal the existence of super-reflections, indicative neither of A-site cation ordering nor of octahedral tilting in the KNN-3%Sb textured ceramics.

This work was financially supported by the National Science Foundation (Materials World Network) DMR-0806592 and by the Department of Energy under DE-FG02-07ER46480. J.Y. would like to thank the financial support from the China Scholarship Council. Authors give thanks to Dr. W. W. Ge, Dr. Z. K. Xu, Dr. S. Bhattacharyya, and Dr. R. Withers for useful discussions and NCFL in Virginia Tech for the TEM support.

[1]Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, and M. Nakamura, Nature (London) **432**, 84 (2004).
[2]Y. Guo, K. Kakimoto, and H. Ohsato, Appl. Phys. Lett. **85**, 4121 (2004).
[3]S. E. Park and T. R. Shrout, J. Appl. Phys. **82**, 1804 (1997).
[4]S. E. Park, S. Wada, L. E. Cross, and T. R. Shrout, J. Appl. Phys. **86**, 2746 (1999).
[5]D. W. Baker, P. A. Thomas, N. Zhang, and A. M. Glazer, Appl. Phys. Lett. **95**, 091903 (2009).
[6]E. Hollenstein, M. Davis, D. Damjanovic, and N. Setter, Appl. Phys. Lett. **87**, 182905 (2005).
[7]R. Wang, R. Xie, K. Hanada, K. Matsusaki, H. Bando, and M. Itoh, Phys. Status Sol. A **202**, R57 (2005).
[8]Y. Guo, K. Kakimoto, and H. Ohsato, Appl. Phys. Lett. **85**, 4121 (2004).
[9]S. T. Zhang, R. Xia, and T. R. Shrout, J. Electroceram. **19**, 251 (2007).
[10]W. W. Ge, J. F. Li, D. Viehland, Y. F. Chang, and G. L. Messing, Phys. Rev. B **83**, 224110 (2011).
[11]J. Tellier, B. Malic, B. Dkhil, D. Jenko, J. Cilensek, and M. Kosec, Solid State Sci. **11**, 320 (2009).
[12]K. Wang and J. F. Li, Adv. Funct. Mater. **20**, 1924 (2010).
[13]J. Fu, R. Z. Zuo, and Z. K. Xu, Appl. Phys. Lett. **99**, 062901 (2011).
[14]Y. F. Chang, S. F. Poterala, Z. P. Yang, S. Trolier-Mckinstry, and G. L. Messing, Appl. Phys. Lett. **95**, 232905 (2009).
[15]F. Bai, J. F. Li, and D. Viehland, J. Appl. Phys. **97**, 054103 (2005).
[16]R. P. Herber, G. A. Schneider, S. Wagner, and M. J. Hoffmann, Appl. Phys. Lett. **90**, 252905 (2007).
[17]S. J. Zhang, H. J. Lee, C. Ma, and X. L. Tan, J. Am. Ceram. Soc. **94**, 3659 (2011).
[18]Y. Zhou, M. Guo, C. Zhang, and M. Zhang, Ceram. Int. **35**, 3253 (2009).
[19]X. B. Ren, Nat. Mater. **3**, 91 (2004).
[20]L. X. Zhang, W. Chen, and X. B. Ren, Appl. Phys. Lett. **85**, 5658 (2004).
[21]S. Wada, K. Yako, H, Kakemoto, T. Tsurui, and T. Kiguchi, J. Appl. Phys. **98**, 014109 (2005).
[22]S. J. Zhang, N. P. Sherlock, R. J. Meyer, and T. R. Shrout, Appl. Phys. Lett. **94**, 162906 (2009).
[23]Y. Xiang, R. Zhang, and W. W. Cao, Appl. Phys. Lett. **96**, 092902 (2010).
[24]J. J. Yao, L. Yan, W. W. Ge, L. Luo, J. F. Li, D. Viehland, Q. H. Zhang, and H. Luo, Phys. Rev. B **83**, 054107 (2011).
[25]J. H. Gao, D. Z. Xue, Y. Wang, D. Wang, L. X. Zhang, H. J. Wu, S. W. Guo, H. X. Bao, C. Zhou, W. F. Liu, S. Sen, G. Xiao, and X. B. Ren, Appl. Phys. Lett. **99**, 092901 (2011).
[26]D. B. Lin, H. J. Lee, S. J. Zhang, F. Li, Z. R. Li, and Z. Xu, Scr. Mater. **64**, 1149 (2011).
[27]J. J. Yao, N. Monsegue, M. Murayama, W. N. Leng, W. T. Reynolds, Q. H. Zhang, H. S. Luo, J. F. Li, W. W. Ge, and D. Viehland, Appl. Phys. Lett. **100**, 012901 (2012).
[28]W. F. Rao, K. W. Xiao, T. L. Chen, and Y. Wang, Appl. Phys. Lett. **97**, 162901 (2010).
[29]Z. G. Yi, Y. Liu, M. A. Carpenter, J. Schiemer, and R. L. Withers, Dalton Trans. **40**, 5066 (2011).
[30]I. M. Reaney, in Proceedings of Electroceramics V, Portugal, 2–4 September 1996, pp. 441–446.
[31]D. I. Woodward and I. M. Reaney, Acta Cryst. B **61**, 387 (2005).
[32]D. Damjanovic, J. Am. Ceram. Soc. **88**, 2663 (2005).