

Contrasting aging behavior of as-grown and annealed BaTiO₃ single crystals grown by KF-flux technique

Huixin Bao, Lixue Zhang, Yu Wang, WenFeng Liu, Chao Zhou, and Xiaobing Ren^{a)}

Multi-disciplinary Materials Research Center, Xi'an Jiaotong University, Xi'an 710049, China; State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, China; and Ferroic Physics Group, National Institute for Materials Science, Tsukuba, 305-0047 Ibaraki, Japan

(Received 8 August 2007; accepted 7 September 2007; published online 2 October 2007)

Acceptor-doped ferroelectrics generally show a pronounced aging effect. However, the KF-flux-grown BaTiO₃ single crystals, which are known to contain acceptor impurities K⁺, show no aging effect. This exception poses a potential challenge to the current understanding of ferroelectric aging and may provide a clue for reducing aging effect in acceptor-doped ferroelectrics. To solve this puzzle, we compared the ferroelectric and dielectric aging effects of the as-grown and annealed KF-flux-grown BaTiO₃ single crystals. We found that although the as-grown BaTiO₃ showed almost no aging effect, the annealed BaTiO₃ showed clear aging effect. Chemical analysis revealed that the as-grown crystals contain not only acceptor impurity K⁺ but also higher concentration of anion donor F⁻; on the other hand, the annealed crystals contain mostly K⁺, as a result of F⁻ evaporation. Based on defect chemistry analysis and the microscopic mechanism of the aging, the difference in the aging behavior of the two kinds of crystal is fully explained. Our result suggests that besides the thermodynamic driving force due to the symmetry-conforming short-range ordering of point defects, kinetic factors (the mobility of point defects) also play a crucial role in determining whether or not aging appears. Donor doping is an effective way to reduce the aging effect through eliminating mobile oxygen vacancies. © 2007 American Institute of Physics.

[DOI: 10.1063/1.2790480]

Ferroelectric aging is a generally observed phenomenon, and it strongly affects the application of ferroelectric materials.¹⁻³ It manifests itself as a gradual change in physical properties of ferroelectrics with time, such as the appearance of a double hysteresis loop,^{4,5} the decrease in dielectric constant, and piezoelectric constant.³ These aging effects are well studied and are generally ascribed to the existence of acceptor impurity/dopants, which explained either by a boundary effect⁶ or volume effect.^{7,8} Recent study revealed that the aging effect is mainly a volume effect because significant aging has been found even in domain-wall-free samples.⁹

However, there has been a long-standing exception to the above acceptor scenario of aging. Since 1950's, the as-grown BaTiO₃ single crystals grown by KF-flux technique, which are known to contain some acceptor K⁺ impurities,^{10,11} have been known to have no sign of aging effect because they always show a normal hysteresis loop.^{12,13} This exception poses a potential challenge to available aging theories and, on the other hand, may provide a clue on how to reduce the aging effect in acceptor-doped ferroelectrics.

To solve the puzzle, in the present study, we compared the aging behavior of as-grown and annealed KF-flux-grown BaTiO₃ single crystals. Interestingly, we found that contrary to the nonexistence of the aging effect in as-grown BaTiO₃, the annealed BaTiO₃ shows obvious aging. We shall show that such a different aging behavior arises from a major difference in their defect chemistry, which makes aging *kinetically impossible* in the as-grown state. Our work has the implications for a deeper understanding on the nature of ag-

ing and on how to control or reduce the aging effect.

In this study, KF-flux-grown BaTiO₃ (BT) single crystals (with a triangular shape with 4 mm edge length, which were prepared by the Remeika-Devries method^{12,14}) were subdivided into three groups. Group 1 [hereafter BT-0 h] was the as-grown crystals; group 2 (BT-5 h) was the same crystals but annealed at 1000 °C for 5 h, and group 3 (BT-10 h) was annealed at 1000 °C for 10 h. Before aging, all the samples (coated with silver electrodes) were heated to 300 °C (above $T_C \sim 115$ °C) and kept for 3 h to remove the aging effect and ensure them to start from unaged states. Then, they were immediately cooled to ferroelectric state (80 °C) and kept for 160 h to achieve a fully aged state. The aging effect was characterized by measuring the change in hysteresis loop (measured at 10 Hz) and dielectric permittivity (measured at 1 kHz) with aging time.

Figure 1 shows the hysteresis loops for the as-grown (BT-0 h) and annealed (BT-5 h, BT-10 h) BaTiO₃ single crystals before and after aging, respectively. Obviously, before aging, all these samples show a normal hysteresis loop. However, after aging their hysteresis loops show a marked difference. After aging at 80 °C for 160 h, BT-0 h shows a hysteresis loop [Fig. 1(a2)] being almost the same as that of its unaged state [Fig. 1(a1)]. This indicates that as-grown sample has virtually no aging effect, confirming the previous observations.^{12,13} By contrast, the BT-5 h sample shows a slightly constricted hysteresis loop [Fig. 1(b2)] and the BT-10 h sample shows a fully developed double hysteresis loop [Fig. 1(c2)]. Therefore, as-grown crystals show no aging effect, but the annealed samples reveal obvious aging effect, which becomes more significant with increasing annealing time at 1000 °C.

^{a)}Electronic mail: ren.xiaobing@nims.go.jp

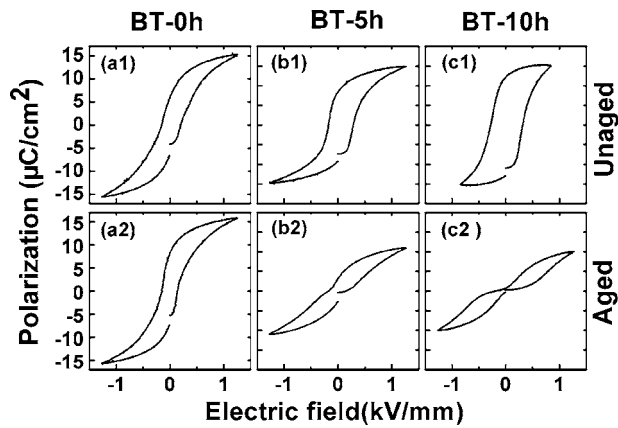


FIG. 1. Contrasting P - E hysteresis loops of as-grown (BT-0 h) and annealed (BT-5 h, BT-10 h) BaTiO_3 single crystals. (a1) BT-0 h, (b1) BT-5 h, and (c1) BT-10 h show their hysteresis loops before aging; (a2) BT-0 h, (b2) BT-5 h, and (c2) BT-10 h show their hysteresis loops after aging at 80°C for 160 h.

Figure 2 shows a comparison of the dielectric aging effect for BT-0 h, BT-5 h, and BT-10 h. It can be seen that the dielectric permittivity of BT-0 h keeps almost constant with the increase of aging time. However, the dielectric permittivity of BT-5 h and BT-10 h gradually decreases with time, and the BT-10 h shows a more significant decrease than BT-5 h does. Therefore, dielectric aging effect exists only in annealed samples and the effect becomes stronger for samples with longer annealing time. This result is fully consistent with the aging effect shown in the hysteresis loop measurement (Fig. 1).

The contrasting aging behavior between the as-grown and annealed BaTiO_3 indicates that there must be an inherent difference between them. To reveal such a difference, we used Shimazu's x-ray fluorescence analyser XRF-1800 to quantitatively analyze the composition of the crystals studied, and the result is surprising, as shown in Fig. 3: BT-0 h actually contains not just K^+ but a richer F^- impurities; BT-5 h also contains both K^+ and F^- , but richer in K^+ ; and BT-10 h contains K^+ only. Clearly, both K^+ and F^- impurities are introduced into the BaTiO_3 crystal from the KF flux during crystal growth. Figure 3 reveals an interesting fact that both impurities F^- and K^+ in the BaTiO_3 crystals seem to evaporate during high temperature annealing, but F^- has a much stronger evaporation tendency than K^+ does, and it virtually vanishes after 10 h annealing at 1000°C , whereas K^+ concentration shows only a slight decrease. Therefore, we

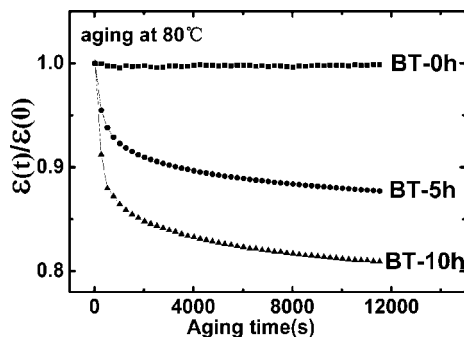


FIG. 2. Dielectric aging behavior of as-grown (BT-0 h) and annealed (BT-5 h, BT-10 h) BaTiO_3 single crystals. $\varepsilon(0)$ is the dielectric permittivity of unaged sample and $\varepsilon(t)$ is the dielectric permittivity at t (aging time). $\varepsilon(t)/\varepsilon(0)$ is a measure of relative change of permittivity.

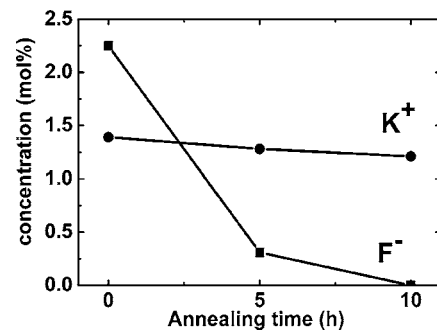


FIG. 3. Impurity (K^+ and F^-) content of KF-grown BaTiO_3 single crystal as a function of annealing time at 1000°C . The point at 0, 5, and 10 h represents the as-grown (BT-0 h) and annealed (BT-5 h, BT-10 h) samples, respectively.

can clearly see that the inherent difference among the three samples lies in their composition difference. In the following, we shall show that the difference in the relative concentration of K^+ (as acceptor) and F^- (as donor) of the three kinds of crystals will generate a fundamental difference in their defect chemistry, and such a difference determines their different aging behaviors.

First, we discuss the simplest case of BT-10 h, which contains acceptor impurity K^+ only. Acceptor K^+ substitutes for Ba^{2+} [denoted as K'_{Ba} (Ref. 15)] and creates O^{2-} vacancies (V''_{O}) to keep charge neutrality. Thus, defect complex $\text{K}'_{\text{Ba}}-\text{V}''_{\text{O}}$ is formed.¹⁵ This is a standard situation for acceptor doping on A site; thus, the aging effect is expected to occur. Our previous studies^{4,5} have given a microscopic explanation for the aging effect associated with acceptor doping on B site (such as Mn^{3+} doping) based on the symmetry-conforming short-range order (SC-SRO) principle of point defects.^{16,17} Now in Fig. 4(a), we provide an explanation for the aging associated with A-site acceptor doping based on the same principle. Above the Curie temperature T_C , the symmetry of the probabilities of finding O^{2-} vacancies in the oxygen site (1–12) around a given acceptor K^+ locating at site 0 is cubic so as to follow the cubic crystal symmetry [Fig. 4(a1)], according to the SC-SRO principle.^{4,16–18} Immediately after cooling down to the polar tetragonal ferroelectric state, the defect symmetry remains cubic [Fig. 4(a2)] because the change of defect symmetry is forbidden during such a diffusionless transition.⁴ As a result, the system reaches an unstable situation that the polar tetragonal crystal symmetry hosts a cubic defect symmetry, and thus there is a driving force to “correct” the defect symmetry into a polar tetragonal one. This is the thermodynamic driving force for aging. During aging in the ferroelectric phase, O^{2-} vacancies will gradually migrate from sites (5–12) to sites (1–4), resulting in a polar tetragonal defect symmetry that follows the polar tetragonal crystal symmetry and a defect dipole \mathbf{P}_D parallel to the spontaneous polarization direction \mathbf{P}_S [Fig. 4(a3)]. The existence of \mathbf{P}_D stabilizes the existing domains so that (1) there is a restoring force to recover the original domain state [Fig. 4(a3)] after a field-induced domain switching [Fig. 4(a4)], and (2) \mathbf{P}_D makes domain-wall motion more difficult.⁹ The first effect explains the observed double loop in Fig. 1(c2) for BT-10 h and the second effect explains the observed permittivity decrease during aging for BT-10 h (Fig. 2) because the domain-wall contribution to permittivity gradually decreases with aging.

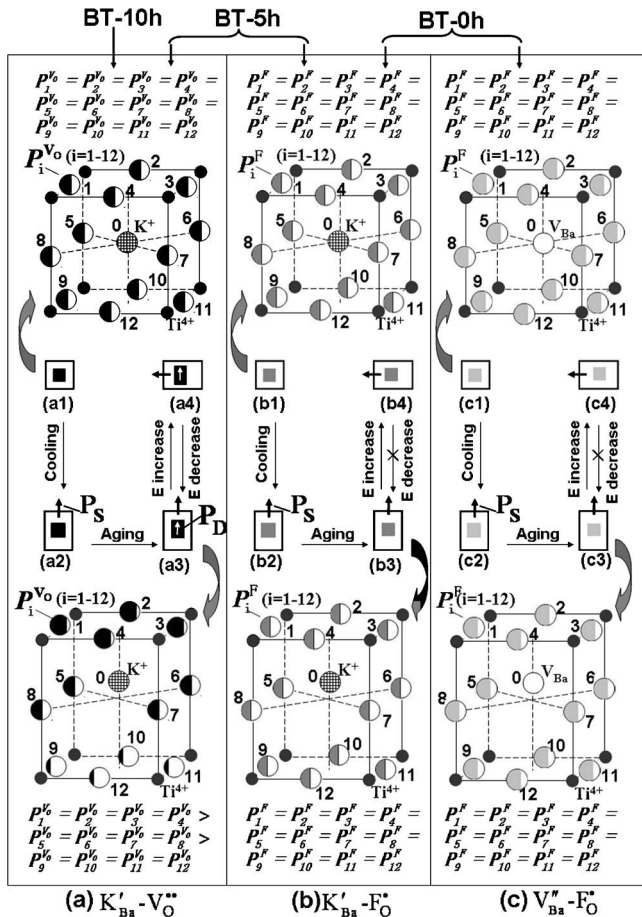


FIG. 4. Microscopic mechanism of the aging effect in BaTiO₃ single crystals associated with defect complexes (a) K'_{Ba}-V_O, (b) K'_{Ba}-F_O, and (c) V'_{Ba}-F_O, respectively. (a1), (b1), and (c1): equilibrium paraelectric state; (a2), (b2), and (c2): unaged ferroelectric state; (a3), (b3), and (c3): ferroelectric state after aged; and (a4), (b4), and (c4): the ferroelectric state after a domain switching by an electric field. $P_i^{V_O}$ is the conditional probability of finding an oxygen vacancy at sites (1–12) around a given acceptor K⁺ at site 0. $P_i^{F^-}$ is the conditional probability of finding F⁻ ions at sites (1–12) around a given acceptor K⁺ or Ba²⁺ vacancy at site 0. The defect symmetry is defined by the symmetry of the $P_i^{V_O}$ or $P_i^{F^-}$, as shown in the figures. Large squares/rectangles represent crystal symmetry and small squares/rectangles represent defect symmetry.

Next, we discuss the as-grown sample (BT-0 h), which contains K⁺ ions and a higher concentration of F⁻ ions, as shown in Fig. 3. Since F⁻ ions substitute for O²⁻ ions (denoted as F_O), they act as anion donor (a situation rare in ferroelectrics). Therefore, BT-0 h is a hybrid-doped sample. As K'_{Ba} and F_O have opposite effective charge, they attract each other during crystal growth and tend to form to defect complex K'_{Ba}-F_O in the BaTiO₃ matrix. The excess F⁻, on the other hand, will be compensated by cation (Ti⁴⁺ or Ba²⁺) vacancies. Therefore, BT-0 h sample contains two kinds of defect complex, K'_{Ba}-F_O and F_O-V_{cation}, but without O²⁻ vacancies. In such a case, although from thermodynamic consideration there is a driving force for aging, being the same as the case of K'_{Ba}-V_O complex as discussed above, the absence of O²⁻ vacancies renders aging kinetically impossible. The reason is given in the following.

We consider the case of short-range ordering of K'_{Ba}-F_O complex in relation to ferroelectric transition and aging [Fig. 4(b)]. In the paraelectric state [Fig. 4(b1)], there is an equal probability of finding F⁻ in oxygen site (1–12) around a given K⁺. Thus, the defect symmetry is cubic, following the

cubic crystal symmetry. After cooling to ferroelectric phase, the crystal symmetry abruptly changes to polar tetragonal while the defect symmetry remains cubic [Fig. 4(b2)]. Following the SC-SRO principle, there is a thermodynamic driving force to change the defect symmetry into polar tetragonal through migration of F⁻ ions from sites (5–12) to sites (1–4). However, kinetically F⁻ migration is impossible at the aging temperature because such migration requires some vacant sites (O²⁻ vacancies) for exchanging ions; but there are no oxygen vacancies in this case. Thus, defect symmetry is forced to keep cubic throughout the aging process, and there is no P_D formed in this process [Fig. 4(b3)]. For the short-range ordering of F_O-V_{cation} complex, the same conclusion is reached following the same reasoning, as shown in Fig. 4(c) (which shows the case for F_O-V_{Ti}, but the same is true for F_O-V_{Ba}); that is, aging is thermodynamically possible but kinetically forbidden because cation vacancies are known to be immobile at the aging temperature² and F⁻ cannot migrate without oxygen vacancies. As a result, for both K'_{Ba}-F_O and F_O-V_{cation} complexes in BT-0 h, defect symmetry remains cubic and no P_D is formed during aging to stabilize the existing domains and to restrain the domain-wall motion. Consequently, there is no driving force for reversible domain switching after a forced domain switching, as shown in Figs. 4(b4) and 4(c4); thus, BT-0 h shows a normal hysteresis loop even after aging, and its permittivity is also not affected by aging, i.e., it shows no aging effect. Therefore, the nonexistence of aging in BT-0 h is caused by a kinetic limitation (the lack of mobile defects such as O²⁻ vacancies).

Finally, for BT-5 h, which has more K⁺ than F⁻, both K'_{Ba}-F_O and K'_{Ba}-V_O complexes exist according to defect chemistry analysis. Following the above analysis, it is easy to deduce that BT-5 h shows a weaker aging effect, because it contains only a smaller number of K'_{Ba}-V_O, which contributes to aging effect (as shown in Fig. 4). This explains the observed weak aging in hysteresis loop [Fig. 1(b)] and in dielectric permittivity (Fig. 2).

The authors thank L. Yang, X. D. Ding, D. Z. Xue, and J. H. Gao for helpful discussions. This work was supported by Kakenhi of JSPS, the NSFC (50720145101 and 50702042), the National Basic Research Program of China (2004CB619303), and the 111 Project of China.

¹F. Jona and G. Shirane, *Ferroelectric Crystals* (Macmillan, New York, 1962), p. 209.

²K. Uchino, *Ferroelectric Device* (Dekker, New York, 2000), p. 279.

³W. A. Schulze and K. Ogino, *Ferroelectrics* **87**, 361 (1988).

⁴X. Ren, *Nat. Mater.* **3**, 91 (2004).

⁵L. X. Zhang and X. Ren, *Phys. Rev. B* **71**, 174108 (2005).

⁶K. Carl and K. H. Hardt, *Ferroelectrics* **17**, 473 (1978).

⁷P. V. Lambeck and G. H. Jonker, *J. Phys. Chem. Solids* **47**, 453 (1986).

⁸U. Robels and G. Arlt, *J. Appl. Phys.* **73**, 3454 (1993).

⁹L. X. Zhang and X. Ren, *Phys. Rev. B* **73**, 094121 (2006).

¹⁰G. Godefroy, P. Lompere, C. Dumas, and H. Arend, *Mater. Res. Bull.* **12**, 165 (1977).

¹¹Y. Akishige, T. Michiie, and T. Tsunogae, *Ferroelectrics* **269**, 249 (2002).

¹²J. P. Remeika, *J. Am. Ceram. Soc.* **76**, 940 (1954).

¹³W. J. Merz, *Phys. Rev.* **91**, 513 (1953).

¹⁴R. C. Devries, *J. Am. Ceram. Soc.* **42**, 547 (1959).

¹⁵D. M. Smith, *The Defect Chemistry of Metal Oxide* (Oxford University Press, New York, 2000), p. 76.

¹⁶X. Ren and K. Otsuka, *Nature (London)* **389**, 579 (1997).

¹⁷X. Ren, and K. Otsuka, *Phys. Rev. Lett.* **85**, 1016 (2000).

¹⁸L. X. Zhang, W. Chen, and X. Ren, *Appl. Phys. Lett.* **85**, 5658 (2004).