

## Temperature-dependent fatigue behaviors of ferroelectric ABO<sub>3</sub>-type and layered perovskite oxide thin films

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The temperature-dependent dielectric and ferroelectric fatigue behaviors of ABO<sub>3</sub>-type perovskite thin films Pb(Zr<sub>0.52</sub>Ti<sub>0.48</sub>)O<sub>3</sub> (PZT) and Pb<sub>0.75</sub>La<sub>0.25</sub>TiO<sub>3</sub> (PLT) and layered Aurivillius thin films SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> (SBT) and Bi<sub>3.25</sub>La<sub>0.75</sub>Ti<sub>3</sub>O<sub>12</sub> (BLT) with Pt electrodes are studied. The improved fatigue resistance of PZT and PLT at a low temperature can be explained by the defect-induced suppression of domain switch/nucleation near the film/electrode interface, which requires a long-range diffusion of defects and charges. It is argued that the fatigue effect of SBT and BLT is attributed to the competition between domain-wall pinning and depinning. The perovskitelike slabs and/or (Bi<sub>2</sub>O<sub>2</sub>)<sup>2+</sup> layers act as barriers for long-range diffusion of defects and charges, resulting in localization of the defects and charges. Thus, the fatigued SBT and BLT can be easily rejuvenated by a high electric field over a wide temperature range. © 2004 American Institute of Physics.  
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Among the ferroelectric materials, two families of perovskites are currently classified according to their fatigue resistance on Pt electrodes: (i) Thin films showing poor fatigue resistance, such as Pb(Zr<sub>0.52</sub>Ti<sub>0.48</sub>)O<sub>3</sub> (PZT), Pb<sub>0.75</sub>La<sub>0.25</sub>TiO<sub>3</sub> (PLT), (Ba,Sr)TiO<sub>3</sub> (BST), BaTiO<sub>3</sub>, and Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> (BTO) and (ii) thin films showing superior fatigue resistance, such as Sr<sub>2</sub>BiTi<sub>2</sub>O<sub>9</sub> (SBT), (BiNd)<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> (BNT), and Bi<sub>3.25</sub>La<sub>0.75</sub>Ti<sub>3</sub>O<sub>12</sub> (BLT).<sup>1</sup> With metallic Pt as electrodes, those ABO<sub>3</sub>-type thin films as well as BTO show poor fatigue resistance performance, while their performance can be improved if conductive oxide is chosen as the electrodes.<sup>1-4</sup> The superior fatigue resistance of SBT, BNT, and BLT films with Pt electrodes may be due to the absence of interfacial layer during polarization reversal.<sup>1,5,6</sup>

It is well established that the ferroelectric fatigue is essentially related to the diffusion of defects and charges (typically oxygen vacancies) in the lattice. One may argue that the low-temperature (*T*) fatigue effect should be weaker than the high-*T* one due to the significantly suppressed defect diffusion when *T* decreases. This may be true for ABO<sub>3</sub>-type perovskite thin films as well as BTO with Pt electrodes. The long-range diffusion of the defects driven by the external electric field enables an aggregation of defects and charges in the film/electrode interfacial layers during the fatigue test sequence, which prohibits nucleation of domains and/or forms screening electric fields. Nevertheless, for SBT, BNT, and BLT thin films, the defect diffusion becomes different from that in ABO<sub>3</sub>-type thin films, because the stable perovskitelike slabs and/or (Bi<sub>2</sub>O<sub>2</sub>)<sup>2+</sup> layers act as natural barriers for long-range diffusion of these defects.<sup>7,8</sup> Thus, the pinning of domains is mainly imposed by those local aggregates of defects between neighboring slabs or (Bi<sub>2</sub>O<sub>2</sub>)<sup>2+</sup> layers. In order to check the mechanisms proposed above, we would like to study the *T*-dependent ferroelectric fatigue be-

haviors of PZT, PLT, SBT, and BLT thin films with Pt electrodes in this letter.

All of our films were deposited on a Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/Si substrate, and thin Pt dots of 200 μm in diameters were deposited to form top electrodes. The PZT-MOD (365 nm), SBT-MOD (660 nm), and BLT-MOD (660 nm) were prepared by metalorganic decomposition (MOD) and annealed at 700 °C, 650 °C, and 700 °C in an oxygen ambient, respectively, where the number in the bracket indicates the film thickness. While PLT-PLD (430 nm), SBT-PLD (377 nm), and BLT-PLD (240 nm) were prepared by pulsed laser deposition (PLD) and annealed at 700 °C, 650 °C, and 700 °C in an oxygen ambient, respectively. All procedures of preparation were optimized in terms of enhanced crystallinity and electrical property, and details of the preparation description were reported elsewhere.<sup>5,6,9</sup> The SBT-MOD and SBT-PLD films, checked by an x-ray diffraction method with Cu *K*α radiation, show preferred (115) orientation, while BLT-MOD and BLT-PLD films show preferred (117) orientation. After the samples were packaged in a temperature-controlled vacuum chamber (20 Pa) with a shielded cable connecting to the top Pt electrodes, the ferroelectric properties of the films were measured with a RT66A ferroelectric tester from Radiant Technologies Inc. and their dielectric properties were measured with an impedance analyzer HP4294A from Agilent Technologies Inc. In addition, the as-prepared thin films were fatigued by using a bipolar pulse with pulsed width of 8.6 μs and period of 20 μs, and the nonvolatile components of the switched polarization measured after the *N*th switching cycle are expressed as  $P_{NV}(N) (= P^* - P^\wedge)$  or  $P_{-NV}(N) (= -P^* - (-P^\wedge))$ , where  $P^*$  and  $P^\wedge$  refer to the pulsed charge measurement by the RT66A.

First, the ferroelectric *P*-*V* loops and dielectric *C*-*V* curves of the as-prepared thin films were measured. As a typical example, only the data of BLT-PLD are introduced. Figure 1 shows the *P*-*V* loops with  $V_{AMP}=19$  V, where  $V_{AMP}$  is the amplitude of the voltage pulses for *P*-*V* loops

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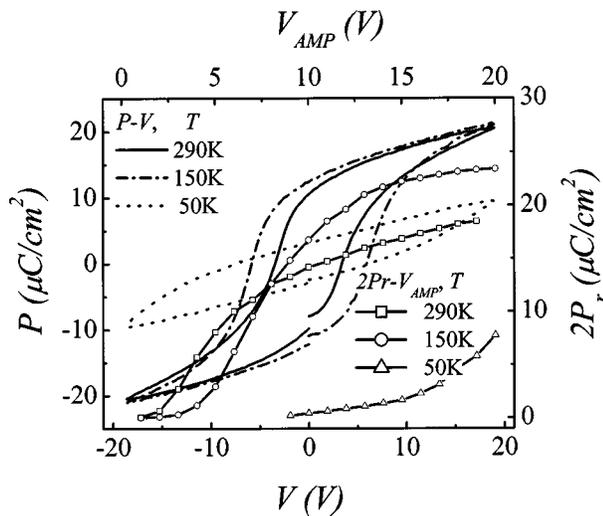


FIG. 1.  $P$ - $V$  hysteresis loops and  $2P_r$ - $V_{AMP}$  curves for BLT-PLD at various temperatures.

test. When  $T$  decreases, the saturated loop shows a larger coercive voltage ( $V_c$ ) and bigger remnant polarization ( $P_r$ ), and the unsaturated loop shows a smaller  $P_r$ . In addition, the dielectric constant ( $\epsilon$ ) and loss ( $\tan \delta$ ) as a function of dc-biased voltage are also measured at 0.05 MHz and ac signal of 50 mV at several temperatures. When  $T$  is low, both  $\epsilon$  and  $\tan \delta$  become small.

The fatigue behaviors for PZT-MOD and PLT-PLD thin films with Pt as electrodes at different  $T$  are shown in Figs. 2(a) and 2(b), respectively. At room temperature, the fatigue effect is remarkable but this effect is significantly suppressed with decreasing  $T$ , as reported earlier.<sup>10-12</sup> As shown in Fig. 2(b), after  $N \sim 10^{10}$ , where  $N$  is the number of switching cycles,  $P_{NV}$  and  $P_{-NV}$  of PLT-PLD thin films show  $\sim 38\%$  reduction at 296 K and  $V_p = 16$  V, where  $V_p$  is the amplitude of the voltage pulses for fatigue test. But at  $T = 95$  K and  $V_p = 12$  V,  $P_{NV}$  and  $P_{-NV}$  are almost constant. Although the fatigue mechanisms for PZT and PLT, such as prohibition of domain nucleation/switching and formation of the screening electric field, remain controversial,<sup>1,12</sup> it is basically believed that they are always due to the aggregation of defect charges in the film/electrode layers by long-range diffusion during the switching cycle sequence, which was demonstrated by the very recent work of Jiang *et al.*<sup>13</sup> The numerical simulation performed by Scott *et al.* is in excellent agreement with the experimental data in Fig. 2.<sup>12-15</sup> However, it is revealed that the degraded polarization due to the fatigue cannot be rejuvenated by only five switching cycles with a high-voltage  $V_{AMP} \sim V_S$ , the saturated voltage, unless external activation such as illumination is applied.<sup>16</sup> To explain these effects, one may consult the model mentioned above. During the switching cycles sequence, the serious degradation of  $P_s$  and  $P_r$  at room temperature is due to the long-range diffusion of defect charges across the film thickness and congregation of them in the film/electrode layers. On one hand, a decreasing  $T$  significantly suppresses the diffusion of defect charges, so that the fatigue effect will be remarkably suppressed. On the other hand, a rejuvenation of the degraded polarization under a much higher electric field requires a recovery of the distribution of defects back to their original distribution, which is kinetically difficult.

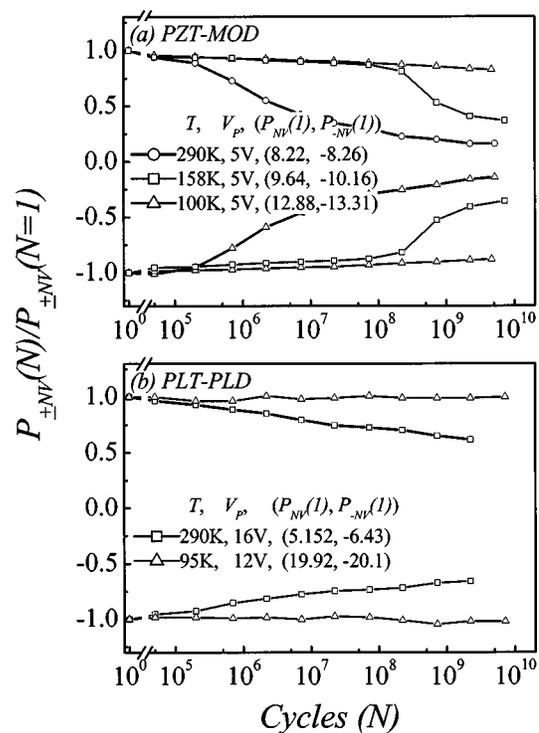


FIG. 2. Normalized  $P_{NV}$  and  $P_{-NV}$  plotted against  $N$  for (a) PZT-MOD and (b) PLT-PLD films. Here,  $P_{NV}(1)$  and  $P_{-NV}(1)$  are data measured after the first switching cycle.

For SBT and BLT thin films, the fatigue resistance performance is excellent at room temperature,<sup>7,8,16</sup> and is also confirmed in our experiments over a wide  $T$  range. In earlier studies, three possible mechanisms were proposed for SBT and BLT thin films with Pt electrodes: (1) The oxygen stability of perovskitelike slabs being favored by Bi-free environment,<sup>7</sup> (2) the self-regulating  $(Bi_2O_2)^{2+}$  layer compensating for space charges near the Pt electrodes,<sup>8</sup> (3) domain-wall depinning in balance with domain wall pinning.<sup>16</sup> In fact, the three mechanisms are intrinsically consistent from one and another. Mechanisms (1) and/or (2) are the reasons for mechanism (3). Because the defect charges need to overcome the barriers formed by  $(Bi_2O_2)^{2+}$  layers and/or the stable perovskitelike slabs, they can hardly diffuse toward the electrode/film interface. Instead, they can only pin the domains locally. Also because of the suppression of the long-range defect aggregation, the density of defect charges locally trapped cannot be high. Therefore, the pinning of domain walls in SBT and BLT is relatively weak, compared to PZT and PLT. One may predict that a rejuvenation of the fatigued samples under an electric field higher than the field used for the fatigue test is highly possible. That is to say, the domain-wall depinning happens at least as rapidly as the domain-wall pinning, resulting in a fatigue-free behavior. In fact, the above model reasonably explains our experiments at different  $T$ . On the one hand, after  $N \sim 10^{10}$ , the measured loops is deformed due to the slight fatigue. When five switching cycles with  $V_{AMP} \sim V_S$  is applied to the fatigue samples, the initial state of the sample can be completely recovered, i.e., a full rejuvenation, as shown in Fig. 3.<sup>16</sup> If the rejuvenated samples are submitted to the fatigue test again, the measured fatigue data in terms of  $P_{NV}$  and  $P_{-NV}$  as a function of  $N$  perfectly reproduces the data before

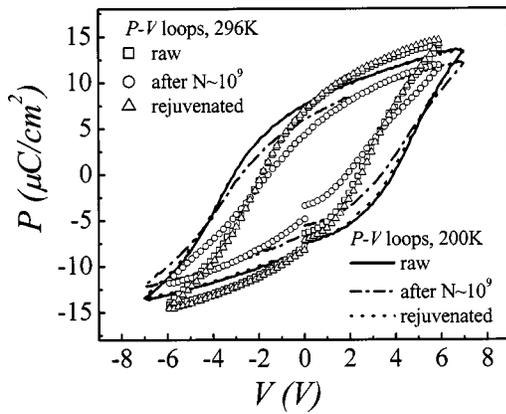


FIG. 3.  $P$ - $V$  loops of three BLT-PLD thin-film samples, i.e. the raw sample, the sample after  $N \sim 10^9$  with  $V_p = 6$  V (or 7 V), as well as the rejuvenated sample after  $N \sim 10^9$  and five switching cycles with  $V_{AMP} = 15$  V, at 296 K (or 200 K), respectively.

the rejuvenation, at both room  $T$  and low  $T$ . On the other hand, the fatigue behaviors depend on  $V_p$ . When  $V_p$  is high, a balance between the domain pinning and depinning is kept so that  $P_{NV}$  and  $P_{-NV}$  show no degradation. With  $V_p$  decreases, the fatigue effect becomes serious.<sup>6</sup> This effect is revealed in our experiment over the whole  $T$  range covered.

For our SBT and BLT films, the dependence of fatigue behaviors on  $V_p$  is weaker at lower  $T$ . In Fig. 4(a), at 296 K and after  $N \sim 10^{10}$ ,  $P_{NV}$  and  $P_{-NV}$  of SBT-MOD thin films increase  $\sim 8\%$  under  $V_p = 10$  V and decrease  $\sim 15\%$  under  $V_p = 5$  V, respectively. However, at  $T = 105$  K,  $P_{NV}$  and  $P_{-NV}$  only decrease 2% under  $V_p = 18$  V and 6.6% under  $V_p = 10$  V, respectively. In Fig. 4(b), at 296 K and after  $N$

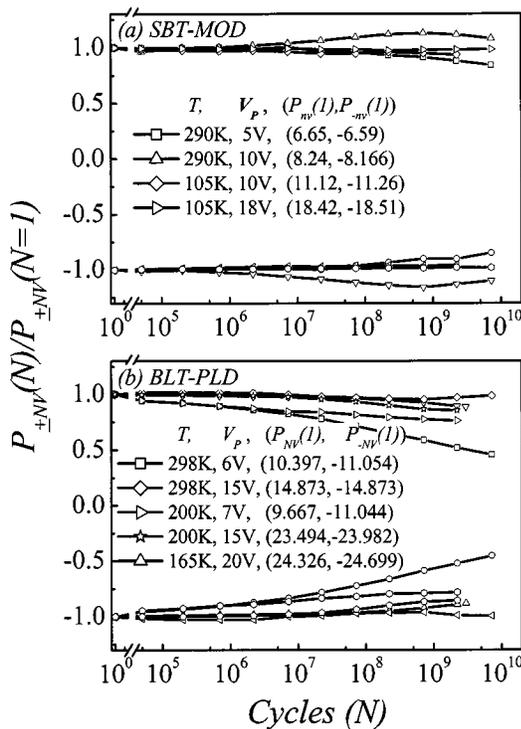


FIG. 4. Normalized  $P_{NV}$  and  $P_{-NV}$  plotted against  $N$  for (a) SBT-MOD and (b) BLT-PLD thin films.

$\sim 2.2 \times 10^9$ ,  $P_{NV}$  and  $P_{-NV}$  of BLT-PLD thin films show no reduction under  $V_p = 15$  V and  $\sim 48\%$  reduction under  $V_p = 6$  V, respectively. However, at 200 K, the reduction of  $P_{NV}$  and  $P_{-NV}$  is  $\sim 21.7\%$  under  $V_p = 7$  V and  $\sim 14.8\%$  under  $V_p = 15$  V, respectively. These experimental data can be explained by the following mechanisms. We suppose  $(P_{NV}(N) - P_{NV}(1))/P_{NV}(1) \propto V_{pin}(T, V_p) - V_{depin}(T, V_p)$ ,<sup>6</sup> where  $V_{pin}(T, V_p)$  and  $V_{depin}(T, V_p)$  are velocities of the pinning and depinning domain walls, respectively. At lower  $T$ ,  $V_{pin}(T, V_p)$  and  $V_{depin}(T, V_p)$  decrease fast due to the more difficulty of the diffusion of defects and charges,<sup>12,17</sup> and thus the dependence of  $V_{pin}(T, V_p) - V_{depin}(T, V_p)$  on  $V_p$  may be weaker.

In conclusion, we have studied the temperature-dependent fatigue behaviors of  $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ ,  $\text{Pb}_{0.75}\text{La}_{0.25}\text{TiO}_3$ ,  $\text{SrBi}_2\text{Ta}_2\text{O}_9$ , and  $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$  thin films with Pt electrodes. For  $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$  and  $\text{Pb}_{0.75}\text{La}_{0.25}\text{TiO}_3$ , the poor/superior fatigue resistance at room/low temperature can be explained by the formation of the film/electrode interface, which requires a long-range diffusion of defects and charges. For  $\text{SrBi}_2\text{Ta}_2\text{O}_9$  and  $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$  thin films, the fatigued samples can be easily rejuvenated by a high electric field because of the localization of the defects and charges. Furthermore, the dependence of fatigue behaviors on the magnitude of the cycling field is weaker at a lower  $T$ .

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