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Frequency response and hysteresis dispersion scaling in ferroelectric $SrBi_2Ta_2O_9$ and $Pb(Ti_{0.48}Zr_{0.52})O_3$ thin films

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Abstract

The dynamic hysteresis of ferroelectric $Pb(Ti_{0.48}Zr_{0.52})O_3$ (PZT) and $Bi_2Sr_2Ta_5O_9$ (SBT) thin films is investigated using the Sawyer–Tower (ST) method, emphasizing the dependence of hysteresis area A against frequency f and amplitude E_0 of applied external electric field. It is revealed that the hysteresis dispersion $A(f)$ under a given E_0 exhibits a single-peaked pattern with power-law tails in the limits of low and high frequency. Based on the mechanism of ferroelectric domain reversal in which the nucleation and growth sequences occur concurrently, a single-parameter dynamic scaling hypothesis on the hysteresis dispersion is proposed and demonstrated for the two types of ferroelectrics. The effective characteristic time for the domain reversal, inversely proportional to the field amplitude E_0, is predicted.

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Keywords: Ferroelectric hysteresis; Hysteresis dispersion; Dynamic scaling

1. Introduction

The mechanism of domain reversal in ferroelectric single-crystals and ceramics represents one of the well-investigated issues in physics of ferroelectricity for a long term [1,2]. The domain reversal sequence, as characterized by ferroelectric hysteresis in a cycle, is driven by an external electric field E once the latter has a component aligned anti-parallel to the spontaneous polarization of the domains and if the component is higher than coercivity E_c. Microscopically, the domain reversal is realized by nucleation of new domains and their growth into the parent domains. In general, the nucleation and growth of new domains occur in a concurrent manner although they were often treated separately [3]. The conventional theories deal with the kinetics of domain reversal driven by a dc electric field while most ferroelectric devices sever under a circumstance of alternative electric (ac) field. However, a dynamic picture of domain reversal under an ac field seems not well understood although a general theory based on the Avrami model was proposed earlier [4,5]. In fact, the nucleation and growth of new domains driven under an AC field show a time-varying feature since the field magnitude is time-varying. Therefore, it should be taken into account the dynamic effect that the reversal kinetics depends on frequency f and amplitude E_0 of the ac field E, say $E = E_0 \cdot \sin(2\pi ft)$, where t is time.

On the other hand, the rapid progress in integrated ferroelectrics stimulates the extensive investigation on ferroelectric thin films for memory applications [2,6]. One issue to be concerned is an experimental testing of the domain reversal as a function of f and E_0 in the regime of ultra-high frequency (10^6∼10^8 Hz). A power-law feature for E_c was demonstrated by measuring the hysteresis [6]. The question arising from these ultra-frequency experiments is whether a complete domain reversal is achieved or not at such high frequency, since the measured polarization is smaller than the saturated value probed at low frequency. If the probed hysteresis does not correspond to a complete domain reversal (unsaturated loop), the real frequency exponent in the power-law for E_c in the limit of high frequency would be larger than the reported exponent in these experiments. It is the purpose of this paper to develop a simple theoretical roadmap by which

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the domain reversal behavior of ferroelectric thin films under ac field over an extra-wide range of frequency can be understood. The idea lies in the well-established theoretical approach for dynamic hysteresis of ferromagnetic solids, where the dependence of magnetic hysteresis on frequency of applied magnetic field was calculated using the Landau thermodynamic concept on phase transitions [7,8].

We study the dynamic evolution of ferroelectric hysteresis for two types of ferroelectric thin films with varying frequency f and amplitude E_0. It is well known that area A of ferroelectric hysteresis represents the energy dissipated during one cycle of domain reversal. Given a fixed E_0 ($>E_c$) for an AC field, area A is small at either low or high f, because of small E_c at low f and low polarization at high f. For an intermediate frequency f_0 at which the domain reversal can be done marginally within an averaged time interval t_0–$1/f_0$, the energy charged for the reversal reaches its maximum. Here one does not care the nucleation and growth as separate sequences, but focuses on the energy dissipation as a symbol for the domain reversal. Therefore, area A appears to be a single-peaked function of f. The function $A(f)$ can be defined as the hysteresis dispersion. If a relationship between t_0 and E_0 can be evaluated from the dispersions at different E_0, the value of E_0 for complete domain reversal at any given f becomes predictable. In this report, we summarize our recent results on two types of ferroelectric thin films within a unified framework [9,10].

2. Experimental details

Ferroelectric $Pb(Ti_{0.48}Zr_{0.52})O_3$ (PZT) and $Bi_2Sr_2Ta_5O_9$ (SBT) thin films, both exhibiting the perovskite structure and so far most widely investigated, are chosen for the present dynamic study. The completely (0 0 1) PZT thin films were prepared using pulsed laser deposition on (0 0 1) $SrTiO_3$ substrates with (0 0 1)-oriented $YBa_2Cu_3O_7$(YBCO) layers as top and bottom electrodes. Details of the sample preparation were given earlier [9]. The SBT thin films were prepared by sol–gel technique on commercial (1 0 0) Si substrates coated with Ti–Pt layers as electrodes. The preferred (1 1 5) orientation of the as-prepared films was identified. Details of the film fabrication and microstructure characterization was reported earlier [10].

The ferroelectric property of the as-prepared PZT and SBT thin films is characterized by the RT6000HVS standard ferroelectric testing unit (Radiant Inc., NM, at virtual ground mode, equivalent frequency 10 Hz), indicating high quality hysteresis loops and low leakage current. Meantime, the loop measured by RT6000HVS is used to calibrate the hysteresis by the standard Sawyer–Tower (ST) method that was applied to probe the dynamic hysteresis at different f and E_0. The ac field is a sine-type signal generated by a function generator [9]. The range of frequency covered in this experiment is $f = 10^{-2}$–10^{7} Hz.

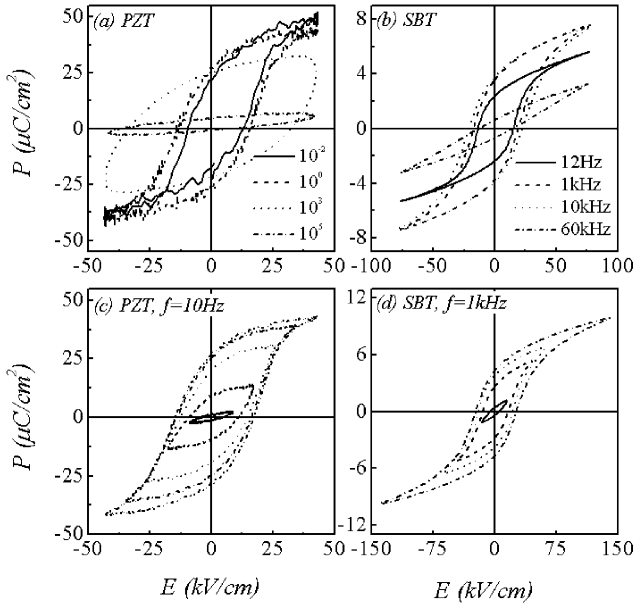

Fig. 1. Hysteresis loops as measured at different frequencies f but fixed amplitude E_0, and at different amplitudes E_0 but fixed frequency f. (a, c) for PZT, and (b, d) for SBT.

3. Results and analysis

In prior to our experiments on the hysteresis dynamics, we compared the loops measured by RT6000HVS and ST methods for both types of thin films. The loops obtained by the two methods keep quite good consistency with each other, particularly for SBT films, identifying the reliability of the data by ST method within the measuring uncertainty. In Fig. 1(a)–(d) the ST-measured hysteresis loops for PZT and SBT thin films, respectively, at fixed E_0 but different f and at fixed f but different E_0 are presented. In general, the response of the hysteresis against varying E_0 and f, respectively is quite similar for PZT and SBT, indicating significant dynamic effect in terms of the strong dependence of the hysteresis pattern and area on both E_0 and f. Given a fixed $E_0 > E_c$ (static coercivity), the loop is well saturated at low f, For PZT, with increasing f polarization at maximum field, P_s, decreases monotonously, while remnant polarization P_r increases first and then falls down. For SBT, it is a little different that both P_s and P_r increase first and then fall down. Looking at E_c (here E_c only refers to the cross point of loop with E-axis), it is enhanced with increasing f for both PZT and SBT. However, the loop (at fixed E_0) can be saturated no longer but a tilted ellipse shrinking slowly with f as f is extremely high, where E_c becomes essentially different from the nominal coercivity, since the domain reversal is not complete anymore. On the other hand, the evolution of hysteresis with increasing E_0 but fixed f is obvious but trivial. The unsaturated ellipse pattern at small E_0 evolves into the saturated and rhombic pattern at large E_0. The parameters P_s, P_r and E_c increase monotonously, but the tendency becomes much weaker as E_0 is large enough.

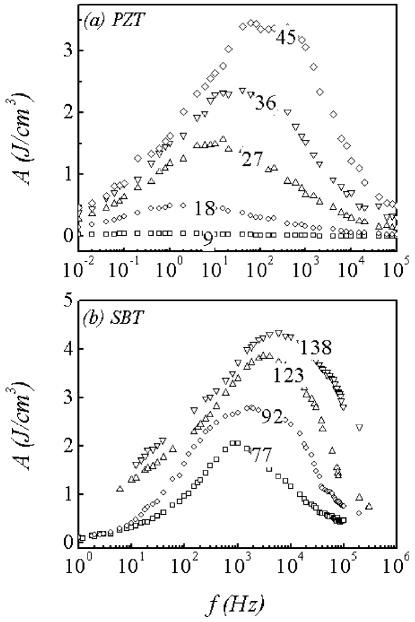

Fig. 2. Hysteresis dispersions at different amplitudes E_0 as numerically indicated. (a) PZT and (b) SBT.

In a qualitative sense, one is allowed to conclude that the maximum area A_{max} is reached at $f = f_0$ at which the domain reversal is done in a marginal state. As $f > f_0$, the reversal can be completed no longer.

From the measured hysteresis we evaluate the hysteresis dispersion $A(f)$ at different E_0, as shown in Fig. 2(a) for PZT and Fig. 2(b) for SBT, respectively. As mentioned earlier, each dispersion curve appears to be single-peaked, confirming the argument that concurrent nucleation and growth sequences proceed in ferroelectric domain reversal. The peak position, labeled by f_0, shifts towards the high frequency direction with increasing E_0. For such a single-peaked dispersion in spin-like systems such as ferromagnetic solids, much theoretical effort has been devoted to understand the power-laws in the limits of low-f and high-f [11–13]. The Landau phenomenological theory on the dynamic hysteresis for ferromagnetic systems suggests the following power-laws [7]:

$$\begin{aligned} A(f, E_0) &\propto f^{1/3} E_0^{2/3} \quad \text{as } f \Rightarrow 0 \\ A(f, E_0) &\propto f^{-1} E_0^{2} \quad \text{as } f \Rightarrow \infty \end{aligned} \tag{1}$$

Here, the evaluated power-laws for ferroelectric PZT and SBT show form but some delicate difference in the exponent to frequency f. As f is very low, the best fitting yields:

$$A(f, E_0) \propto f^{1/3} E_0^{2/3} \quad \text{for PZT} \tag{2a}$$

$$A(f, E_0) \propto f^{2/3} E_0^{2/3} \quad \text{for SBT} \tag{2b}$$

while the power law in the high frequency limit (>10^5 Hz) takes:

$$A(f, E_0) \propto f^{-1/3} E_0^{2} \quad \text{for PZT and SBT} \tag{3}$$

It is seen that in the low-f regime, $A(f)$ increases with f in a rate higher than the predicted rate in Eq. (1) for SBT, or the same rate for PZT, while this rate for decaying of $A(f)$ in the regime of high-f is lower, in relative to the predicted rate in Eq. (1).

It is generally believed that for a dynamic system of conserved ordering parameter, the time- or space-dependent dynamics of the ordering process may exhibit a dynamic scaling behavior. If such a scaling behavior can be characterized by one scaling parameter, the system dynamics becomes uniquely determined by the dynamics of this scaling variable [14]. Since dispersion $A(f)$ scales the energy for domain reversal and the spontaneous polarization is constant at given constant temperature and pressure, $A(f, E_0)$ may exhibit the dynamic scaling property. Essentially, this scaling behavior if confirmed shows a similarity with the scaling in diffusion-limited phase transformations in alloys. In that case, the spatial distribution function $G(R, t)$ in the Fourier-transform form (structure function) of the second phase shows a single-peaked pattern at time t, where R is the characteristic dimension of the second phase. It is well demonstrated that there exists a characteristic R_0, by which the structure function $G(R, t)$ satisfies the following scaling function once $t > t_0$, a critical time [15,16]:

$$W\left(r = \frac{R}{R_0}\right) = R_0^{-d} G(R, t) \tag{4}$$

where r is the scaling variable and d is the spatial dimensionality. R_0 is defined by the power-averaged integration of $G(R, t)$ over the whole spatial range and follows $R_0 \sim t^{1/d}$ except the early stage. In the other words, if the scaling state is reached, the time-dependent evolution of structure function $G(R, t)$ is uniquely determined by $R_0 \sim t^{1/d}$.

For the dynamic hysteresis of PZT and SBT, dispersion $A(f, E_0)$ would be uniquely determined if the dynamic scaling behavior is confirmed. Therefore, the characteristic time τ_d for the domain reversal must be unique, only dependent of E_0.

To perform the scaling analysis, unfortunately, one notes that the power-averaged integration of $A(f, E_0)$ with respect to f is diverse, due to the power-laws shown in Eqs. (2) and (3). To avoid this divergence, we calculate the power-averaged integration of $A(f, E_0)$ with respect to the logarithmically transformed frequency γ:

$$\begin{aligned} &\gamma = \log(f) \\ &S_n(E_0) = \int_{-\infty}^{\infty} \gamma^n A(\gamma, E_0)\, \mathrm{d}\gamma, \quad n = 1, 2, \ldots \\ &\gamma_n(E_0) = \frac{S_n(E_0)}{S_0(E_0)} \\ &n_2(E_0) = \frac{\gamma_2(E_0)}{\gamma_1^2(E_0)} \\ &\tau_1^{-1} = 10^{\gamma_1} \end{aligned} \tag{5}$$

where S_n is the nth power-averaged integrator of $A(\gamma, E_0)$ which is converged for any finite n, γ_n is the nth frequency variable, n_2 is the scaling parameter. The scaling requires

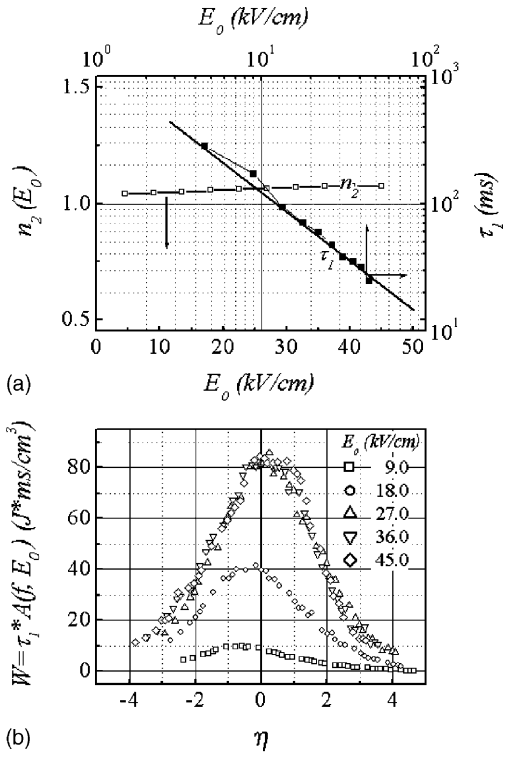

Fig. 3. (a) Scaling parameter n_2 and effective characteristic time τ_1 as a function of amplitude E_0, and (b) scaled hysteresis dispersions for PZT.

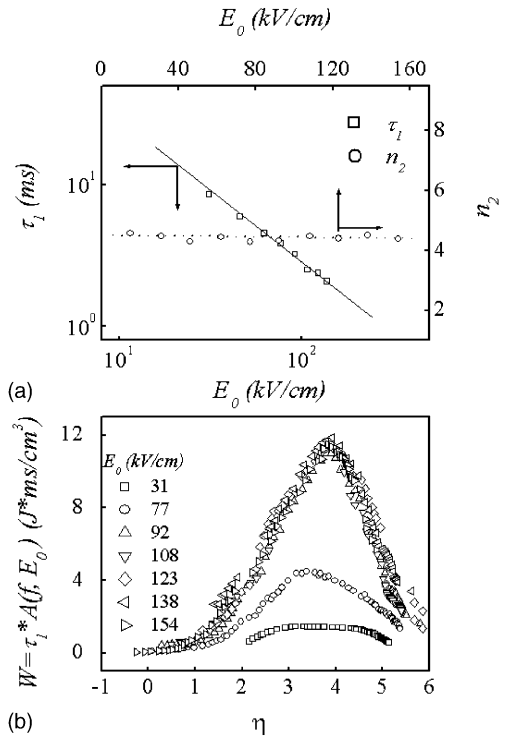

Fig. 4. (a) Scaling parameter n_2 and effective characteristic time τ_1 as a function of amplitude E_0, and (b) scaled hysteresis dispersions for SBT.

a constant n_2 irrelevant of E_0. $\tau_1 = 1/f_1$ is the effective characteristic time that is taken by exponential transform of γ_1. Obviously, τ_1 is proportional to the real characteristic time τ_d for the domain reversal.

In Figs. 3(a) and 4(a) the effective time τ_1 and scaling parameter n_2 as a function of E_0, respectively, for PZT and SBT thin films, is plotted. For both PZT and SBT, no identifiable correlation between n_2 and E_0 is seen within the experimental uncertainties, indicating the scalability of the dispersion $A(f)$. And more interesting is that an inversely proportional relationship between τ_1 and E_0 is revealed, to be shown below.

The simplest scaling function can be formulated as the following form:

$$W(\eta) = \tau_1^{-d} A(\gamma, E_0) \qquad \eta = \log(f\tau_1) \tag{6}$$

where η is the scaling variable and d is the dimensionality with respect to time or frequency ($d \equiv 1$). Consequently, Eq. (6) is simplified into:

$$W(\eta) = \tau_1 A(\gamma, E_0) \qquad \eta = \log(f\tau_1^{-1}) \tag{7}$$

The scaling functions $W(\eta)$ calculated according to Eq. (7) at different E_0 for PZT and SBT are presented in Figs. 3(b) and 4(b), respectively. Except from the cases of small E_0, all rescaled data fall onto the same curve within the experimental uncertainties, demonstrating the single-parameter scaling behavior of the hysteresis dispersion $A(f)$ for both PZT and SBT. And more, based on the confirmed scaling behavior, one has $\tau_1 \sim E_0^{-1/d}$ with $d \equiv 1$, an important conclusion, which predicts co-occurrence of nucleation and growth for the domain reversal sequence in the two types of ferroelectric thin films. With this relation in mind, one can predict conveniently the amplitude of the AC field required for a complete domain reversal at a given frequency.

In fact, relation $\tau_1 \sim E_0^{-1/d}$ with $d \equiv 1$ can be explained in terms of the classical nucleation and growth concept for the domain reversal. No doubt, the generation of ferroelectric hysteresis is related to the domain reversal, as mentioned earlier. According to the classical nucleation concept [13], driven by a dc field, the nucleation rate at different spatial sites satisfies a distribution, and a characteristic time τ_n corresponding to such a distribution can be defined and predicted to follow $\tau_n \sim E^{-2/3}$. As for the growth sequence in which the boundary between new and parent domains move in a rate $1/\tau_g$, where τ_g is the characteristic time for the boundary movement under a given dc field, satisfying $\tau_g \sim E^{-4/3}$, noting the boundary motion rate is spatially inhomogeneous. Taking the domain reversal as the concurrent sequence of domain nucleation and growth, one has the characteristic time τ_d for the domain reversal:

$$\tau_d = \sqrt{\tau_n \tau_g} \propto E^{-1} \tag{8}$$

where the slower sequence controls the domain reversal, which is consistent with the scaling hypothesis confirmed above. Eq. (8) is only an argument for the case of dc field. For the case of ac field, if time τ_d still exists, it can be predicted that given a fixed E_0, the domain reversal can

be fully done once $\tau_d < f^{-1}$ (low frequency) and the measured E_c is small. This event can not be completed if $\tau_d > f^{-1}$ (high frequency), resulting in low P_s and P_r. As $\tau_d \sim f^{-1}$, it is a marginal state at which all domains achieve a complete reversal, so that the energy dissipated during the reversal reaches its maximal. The single-peaked pattern of dispersion $A(f)$ is then qualitatively explained.

The scalability of the hysteresis dispersion for ferroelectric systems (at least PZT and SBT) can find its analogy in spin-like ordering dynamics in magnetic systems. In fact, for soft magnetic systems, the inversely proportional relationship Eq. (8) was confirmed experimentally in 1940s, i.e. the well-known Stematz law [7]. A numerous experimental studies on ferroelectrics regarding on the domain reversal time supported Eq. (8), although the exponent $(1/d)$ may deviate from one in some cases [6]. The earlier theoretical modeling and Monte-Carlo simulations on spin systems also revealed the scalability of the hysteresis dispersion and the applicability of Eq. (8) [17,18].

As E_0 is relatively small, the broken scaling is possibly related to the mode of domain reversal where the contribution of reversible reversal has to be taken into account. At least for ferromagnetic domains, the reversible domain rotation under small E_0 is so quick that no much viscous retardation can be detected unless the frequency is as high as that for magnons. Also should be noted that the scaling analysis does not consider the effect of coercivity which must be much smaller than E_0. Therefore, the scalability can not be true unless E_0 is much larger the static coercivity for a system.

4. Conclusion

In summary, the dynamic hysteresis of ferroelectric PZT and SBT thin films has been investigated using the ST method. The dynamic scaling hypothesis on the dispersion has been proposed and the single-parameter scaling behavior has been demonstrated for the two types of thin films. It is then predicted that the effective characteristic time for the domain reversal is inversely proportional to the amplitude of the external field, well consistent with the experiments on the domain reversal kinetics for ferroelectrics.

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