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Dislocation-density changes upon poling of polycrystalline $BaTiO_3$

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We report evidence for a significant increase of bulk dislocation density upon poling of polycrystalline $BaTiO_3$. The synchrotron high-resolution x-ray-diffraction measurements yield a dislocation density on the order of $10^9/cm^2$ and an associated strain-energy increase of about 20 kJ/m^3. This implies that the application of an external poling field generates defects in the structure and increases the internal stress. Possible consequences in both bulk and thin-film applications include accelerated aging and microcracking. [S0163-1829(99)06005-1]

I. INTRODUCTION

$BaTiO_3$ is perhaps the most-studied ferroelectric. It is particularly interesting for its good ferroelectric properties and relatively high dielectric constant at ambient temperature. Its chemical and mechanical stability in a wide temperature range facilitate easy fabrication of bulk polycrystals and both epitaxial and polycrystalline thin films. Hence, $BaTiO_3$ is used in different applications such as dynamic random-access memory, piezoelectric transducer, thermistor, and actuator. These applications gave impetus to numerous recent studies of the $BaTiO_3$ phase diagram,[1] grain size,[2] dielectric anomaly,[3] oxygen vacancies,[4] and surface.[5] Grain size and surface effects are important for both structure and properties of polycrystalline $BaTiO_3$. It was recognized early on[6] that dielectric properties and crystal structure change for grain size smaller than approximately 1 μm. The changes are associated with a distinct surface layer, reported by Känzig[7] as a tetragonal (ferroelectric) layer on the surface of $BaTiO_3$ above the Curie temperature, where the bulk crystalline structure is cubic. We discuss surface properties and its relation to mechanical distortion[8–10] elsewhere.[11]

The formation of ferroelectric domains is defined by a balance of electrostatic and strain energies with domain-wall energy. Because the poling induces ferroelectric-domain switching and increases polarization, it is expected to increase average ferroelectric-domain size, which in turn should increase the residual strain in grains. It was proposed that this strain is present mainly at grain boundaries.[12] To our knowledge, there were no experimental confirmations of this strain or studies of possible interaction of stresses with crystal defects, especially vacancies and dislocations, which play an important role in surface properties. Both electrical properties and mechanical stability of thin films depend strongly on the residual-stress state and defect concentration. In most ferroelectric thin films, mechanical and thermal stresses were introduced by fabrication and originate from the film-substrate misfit strain. Furthermore, two-dimensional clamping strains shift the temperature of the ferroelectric transition and even induce phases forbidden in the bulk crystals.[1] Another subject that deserves much attention is aging of ferroelectric properties under external electric field. The aging is controlled by interaction of domain walls with defects[13] and any potential changes in stress and defect conditions upon poling are very important. The aim here was to study microstructural changes upon poling in a quantitative manner using high-resolution synchrotron x-ray diffraction. Because neither thickness nor origin of surface layer in $BaTiO_3$ is known, and influence of small grain size on properties is not well understood, we opted to study the subsurface region of bulk large-grain polycrystalline specimens instead of thin films.

II. EXPERIMENT

Specimens and experiment

High-density (99%) $BaTiO_3$ specimens were prepared by isostatic cold pressing of 1.1 μm grain-size $BaTiO_3$ powder at ~200 MPa for 5 min. The compacts were sintered at 1360 °C for 2 h in flowing oxygen and in air with a heating rate of 200 °C/h and a cooling rate of 60 °C/h. The microstructure has shown an average linear-intercept grain size of 52(4) μm. Specimens were poled by an electric field of 1 kV/mm for 1 h at ambient temperature and 80 °C while immersed in silicone oil. Both unpoled and poled pellets were fine polished with 0.3 μm diamond paste.

The specimens were annealed at 250 °C for 4 h to relieve surface stresses. However, preliminary diffraction measure-

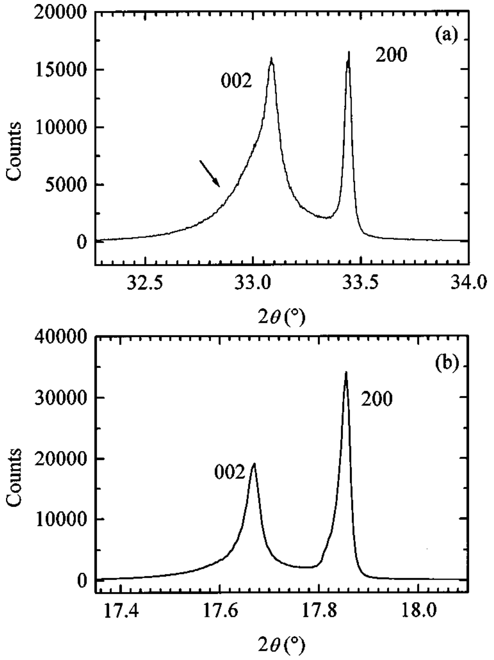


FIG. 1. 002 and 200 diffraction lines of unpoled $BaTiO_3$ at two energies (synchrotron-radiation intensity as a function of Bragg angle θ) (a) 10.7978(2) keV, (b) 20.0168(6) keV.

ments have shown that specimen-preparation conditions drastically influenced the surface of the specimens, which made it impossible to study any subsurface microstructural changes caused by poling. Moreover, diffraction-line broadening caused by microstructural features is relatively small, which emphasizes a need for high-resolution measurements, so that the instrumental broadening can be kept small. Bulk properties can be obtained by neutron diffraction. However, because the lack of resolution would be also a problem for most neutron-diffraction diffractometers, we conducted measurements at the X3B1 powder-diffraction beamline at the National Synchrotron Light Source (Brookhaven National Laboratory) with high-resolution triple-axis geometry.

The powder-diffraction patterns (Fig. 1) at 10.7978(2) keV (attenuation length about 15 μm) clearly revealed additional Bragg reflection that stems from the surface of the specimen.[11] At yet higher energy (20.0168(6) keV, attenuation length about 82 μm), the additional diffraction lines from the surface layer are almost invisible. The relative integrated intensities of 002 and 200 diffraction lines from the bulk are approximately in the 1:2 ratio, as expected for random-orientation powder.

III. RESULTS AND DISCUSSION

A. 90° domain switching

During poling, reorientation and growth of ferroelectric domains occur. In the tetragonal phase, both 90° and 180° domain switches are possible. However, the mechanism of polarization switching is still unknown, especially in polycrystals. It is likely that forward growth occurs first, then side growth of 180° domains, followed by reorientation of 90° domains, as confirmed by *in situ* x-ray diffraction under the variable electric field.[14] Because the polarization vector is along [001], these changes are theoretically trackable by monitoring the relative ratio of $00l$ and $h00$ diffraction-line intensities I:[15]

$$p=\frac{(I_{h00}/I_{00l})_u-(I_{h00}/I_{00l})_p}{(I_{h00}/I_{00l})_u[1+(I_{h00}/I_{00l})_p]}. \tag{1}$$

Here, u and p refer to the unpoled and poled specimen. However, because of Friedel's rule, the 180° domain switching will not affect relative intensities, and this measurement will detect 90° switching only. The 180° switch is energetically less costly because the 180° domain switching is not associated with a change in residual strain, while 90° domain switching changes the state of strain because of slight tetragonal distortion of crystal structure. Our measurements indicate a 4–10% of 90° domain switch, somewhat less than usually reported (Jona and Shirane[16] cite this percentage as 10–12% from different studies). Because our measurements are for the bulk only, they probably confirm that poling effects are more pronounced at the surface,[10] where the 90° domain switching would be less inhibited because the stress must relax.

B. Homogeneous strain

Below the temperature of ferroelectric phase transition, the formation of ferroelectric domains is driven by a need to minimize both the electrostatic and strain energy. Jacobs[17] recently showed for a two-dimensionally constrained ferroelastic[18] that the formation of twins results in nonzero dilatational and shear strains near the boundaries. Arlt[19] discussed the stress relief in ferroelectrics extensively on the basis of phenomenological arguments. He argued that the grain clamping in $BaTiO_3$ causes homogeneous deformation with shear and longitudinal components. According to this model, upon poling, the growth of domains should increase the homogeneous strain component and simultaneously decrease the inhomogeneous component because of fewer 90° domain walls. Homogeneous strains can be calculated from a model for a constrained ellipsoidal grain in an isotropic matrix.[20] To our knowledge, there was no absolute number reported in the literature to date. As a quick estimate, we can place an upper limit on this strain. In the unpoled $BaTiO_3$, the homogeneous-strain component is limited by the spontaneous tetragonal strain, $c/a-1=e_s\approx 1\%$. Under the poling electric field, domains will experience an electrostriction effect. As an estimate, we calculate from the polycrystalline values of piezoelectric coefficients, d_{33} and d_{31}, reported[21] with applied field $E_3=1$ kV/mm, the strain e_c along the c axis and strain e_a along the a axis $e_c=1.91\times 10^{-4}$, $e_a=-0.791\times 10^{-4}$. For a free single ferroelectric domain with a polarization vector along the external field, the relative change of tetragonal strain is

$$\frac{(c/a)(d_{33}-d_{31})/(1+d_{31}E_3)E_3}{e_s}\approx\frac{e_c-e_a}{e_s}. \tag{2}$$

This is almost 3%, which is about three times larger than the spontaneous strain itself for this magnitude of external field. Therefore, we can roughly estimate that the possible strain change should be on the order of 10^{-4}.

The homogeneous strain component is actually caused by elastic incompatibilities of grains oriented in different directions. These strains and associated stresses are usually classified as those of second kind[22] and have been much studied in anisotropic metals and alloys by x-ray and neutron diffraction. A homogeneous elastic strain causes a change in the interplanar spacing that can be discerned by directionally dependent measurements of diffraction-line shifts.[22] We monitored[23] the lattice spacing d as a function of the specimen tilt angle (the $\sin^2 \psi$ method[24]) to detect a possible change in the deviatoric component of elastic strain because measurements of lattice parameters yield only the hydrostatic component. However, we found no differences in either hydrostatic or deviatoric strain components between unpoled and poled specimens by using high-resolution synchrotron-radiation measurements. Thus, any possible homogeneous strain is probably below the detection capabilities of the diffraction method, which we estimate as ~0.006%, that is, better than the expected strain change (0.01%), which was estimated above.

C. Inhomogeneous strain and dislocations

As shown by Arlt,[19] the inhomogeneous strain component is localized at the subgrain and subdomain level near grain boundaries. Pertsev and Arlt[25] introduced a fictitious dislocation density to model the inhomogeneous strain. The spontaneous strain in their model is analogous to the mechanical plastic deformation, for instance, in metals. This facilitates the analysis substantially because models developed for dislocations can be readily applied. They obtained two components of strain/stress fields: a homogeneous volume component extending over the whole grain volume and an inhomogeneous component concentrated near grain boundaries. We argue that dislocations effects are a real origin of inhomogeneous strains in $BaTiO_3$ and that large changes in dislocation density and configuration may occur during poling.[26] The increase of both electrostatic and (homogeneous) strain energy under the external electric field may be accompanied by the creation of crystal defects, especially dislocations. This effect may be dominant along the direction of external electric field, where the electrostriction effect is largest. When the poling field is switched off, a partial domain reversal to minimize the total energy is likely. However, without a driving force for a massive domain-orientation reversal, the strain and electrostatic energy may be lowered by the change in dislocations arrangement, which will in turn relieve stresses caused by an external electric field.

Dislocations can carry charge in ionic crystals. The most likely mechanism in $BaTiO_3$ is that dislocations attract isolated charged vacancies.[27] Thus, additional to elastic interaction between dislocations and point defects, there is a long-range Coulomb interaction, which is confirmed by observations of deformation-induced charge flow without external electric field.[28] Normally, upon mechanical deformation, the charge will be balanced because a homogeneous deformation will cause movement of dislocations of opposite Burgers vectors in opposite directions. However, an inhomogeneous deformation can cause a net flow of dislocations of the same sign of Burgers vector, thus causing a charge unbalance in domains. This may be a possible mechanism to minimize the electrostatic energy during and after the poling. Dislocations may also play important role in movement of 180° domain walls at higher electric fields[29,30] and influence both the dielectric constant and dielectric loss.

D. Diffraction-line-broadening analysis

Lattice distortions that originate from crystal defects cause an inhomogeneous state of strain that results in broadening of diffraction lines. The change of diffraction coherent length (size of the coherently diffracting domains) and domain-size distribution also influences the diffraction line-width. A comprehensive review on this subject was given by Warren.[31] The specifics about this particular approach to diffraction-line-broadening analysis, where the physically broadened profile is modeled by an exact Voigt function, were given in reviews by Balzar.[32,33] To obtain the contribution from only physical origins to line broadening, diffraction-line profiles were corrected for instrumental broadening, which was determined by the measurements of an NIST Standard Reference Material 660 LaB_6. Figure 2 and Table I show the results of least-squares refinements of diffraction patterns obtained at 20.0168(6) keV, where the influence of the surface phase is minimal, but was accounted for. The results include the volume-weighted coherent domain size (VWCDS) and root-mean-square strain (RMSS). There is a large anisotropy of both the VWCDS and RMSS for the unpoled specimen. After poling, the VWCDS is somewhat smaller and RMSS becomes significantly larger. Figure 3 shows domain-size distributions that are more instructive than mere average values given in Table I. The coherently diffracting domain sizes (0.1–0.25 μm) are 3–6 times smaller than the expected values (0.7–0.8 μm) for ferroelectric domains in $BaTiO_3$, which are independent of grain size for 10 μm and larger grain size.[12] This is a known phenomenon: diffraction coherent length reflects subgrain structure, such as dislocation cells, small-angle boundaries, and lattice-stacking or twin faults. Therefore, the domain-size broadening measured by diffraction does not correspond to the size of ferroelectric domains, but is rather an indication of crystal defects. The observation that poling broadens diffraction lines disagrees with results of Seth, Gatins, and Schulze.[10] They observed the sharpening of diffraction lines upon poling, which was explained by the growth of ferroelectric domains. However, such sharpening is not likely to occur, even if the broadening on a scale of the ferroelectric domain is considered because the size of 90° domains will decrease, which will augment the diffraction-line broadening. Conversely, the increase in size of 180° domains is not likely to counteract this effect because size-broadening effects become much less important for coherent-domain size larger than about 100 nm. To better understand this, Fig. 4 presents a schematic representation of likely domain changes upon poling. Because in Bragg-Brentano symmetrical geometry, the diffraction vector is perpendicular to the specimen surface, only the crystallographic planes parallel to the specimen surface contribute to the measured intensity and both the VWCDS and RMSS are measured along the diffraction vector. Therefore, intensity in [001] is contributed only by *c* domains and in [100] by *a* domains. According to our measurements, less than 10% of 90° domains switch, which means that 90° wall motion was limited. This is confirmed

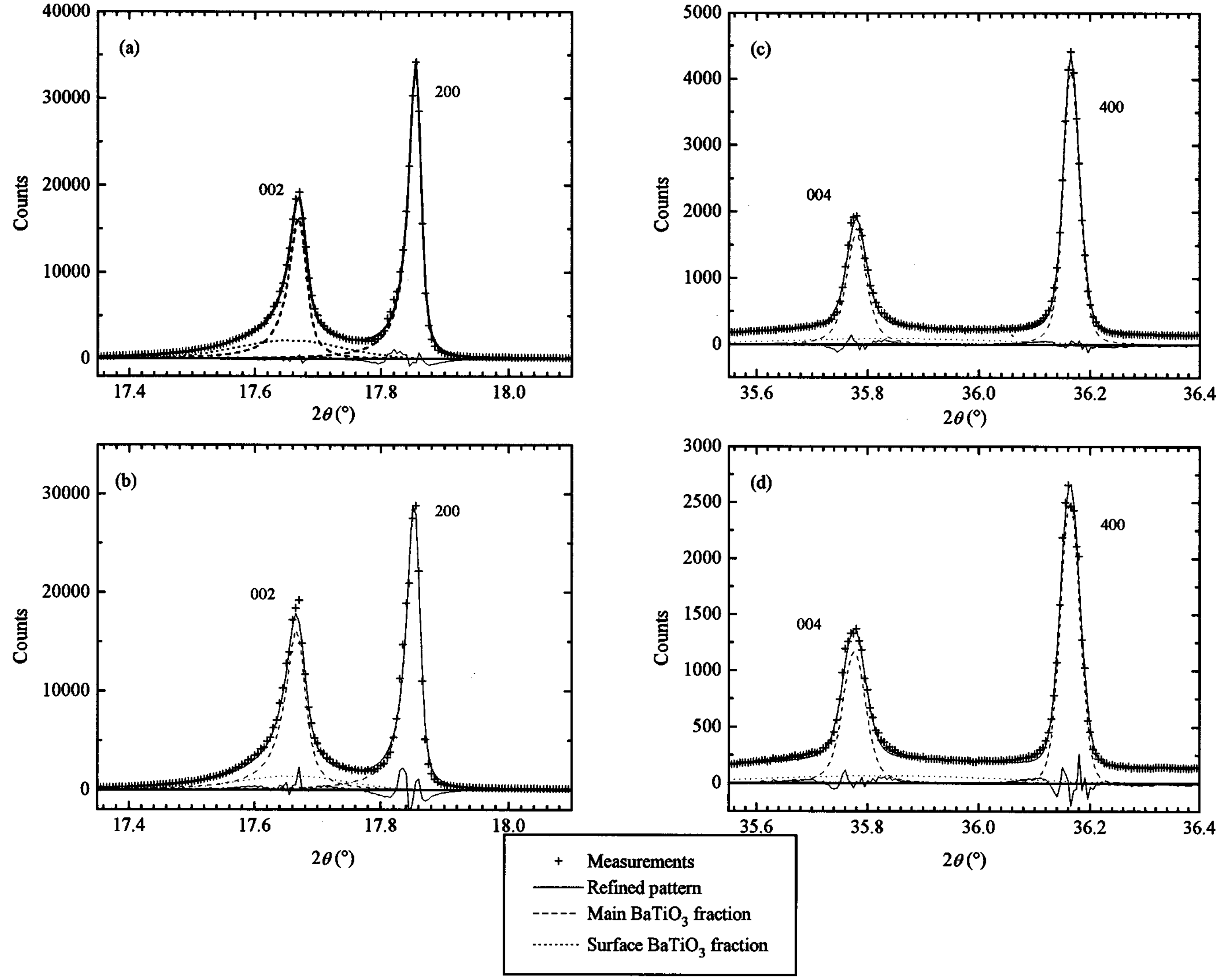


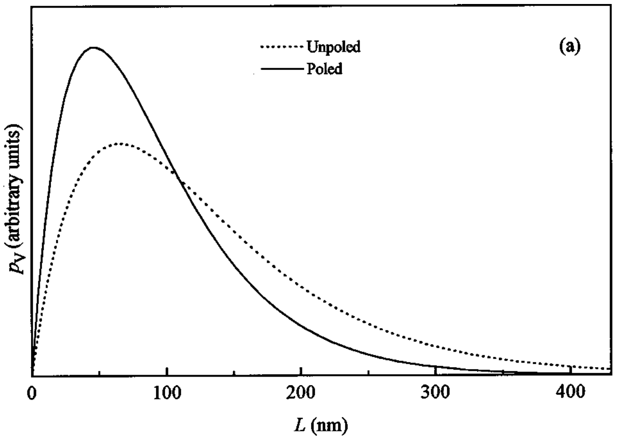
FIG. 2. Fits of 20.0168(6) keV data as a function of Bragg angle θ. The refined pattern is a convolution of pre-determined instrumental-broadening profile and an assumed Voigt function that models the physical broadening. (a) 002 and 200 diffraction lines of unpoled $BaTiO_3$, (b) 002 and 200 diffraction lines of poled $BaTiO_3$, (c) 004 and 400 diffraction lines of unpoled $BaTiO_3$, (d) 004 and 400 diffraction lines of poled $BaTiO_3$.

by the fact that the [100] domain-size distribution shifts only slightly toward smaller domain size. Similarly, the *c* domain-size dimension perpendicular to the surface will be enlarged only slightly by the 90° wall motion or 180° wall side motion; only its forward growth would be expected to increase the VWCDS substantially. However, forward growth would require 90° wall motion that is limited by grain boundaries in the polycrystal bulk. This mechanism is much more impor-

TABLE I. Results of line-broadening analysis (volume-weighted coherent domain size $\langle D\rangle_V$ and root-mean-square strain $\langle\epsilon^2\rangle^{1/2}$ averaged over $\langle D\rangle_V$) and dislocation densities ρ_D and ρ_ϵ that follow from the respective values of $\langle D\rangle_V$ and $\langle\epsilon^2\rangle$ for unpoled and poled $BaTiO_3$ specimens.

	Direction	$\langle D\rangle_V$ (nm)	$\langle\epsilon^2\rangle^{1/2}$[a] ($10^{-4}$)	ρ_D (10^9/cm^2)	ρ_ϵ (10^9/cm^2)
Unpoled	[001]	130(6)	1.2(8)	5.9(6)	0.3(3)
	[100]	252(24)	0.0(2)	1.6(3)	0
Poled	[001]	92(13)	3.1(11)	12(3)	0.8(7)
	[100]	244(26)	3.0(2)	1.7(4)	0.7(1)

[a] Root-mean-square strain is generally a function of averaging distance perpendicular to diffracting planes in this diffraction-line-broadening method. Here, it was obtained to be a constant, which is a special case for some defect distributions (see discussion in Ref. 44).



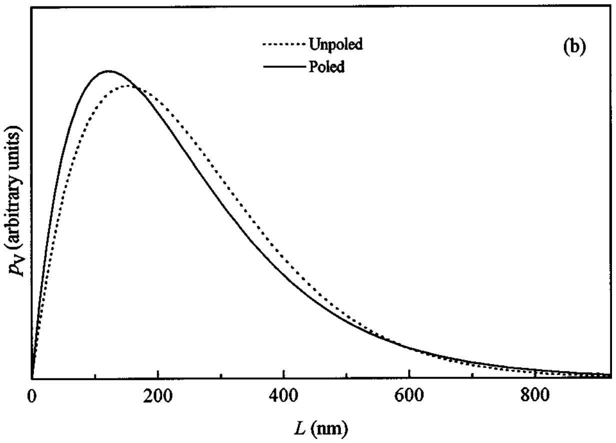
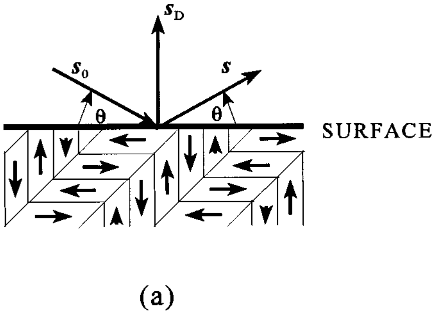


FIG. 3. Volume-weighted domain-size-distribution functions p_v as a function of coherent lengths L in grains for unpoled and poled $BaTiO_3$ specimen [20.0168(6) keV data] (a) along [001], (b) along [100].

tant in monocrystals, where the forward domain growth starts from the surface layer and propagates through the crystal thickness, as shown by Janovec.[34]

There is little change in domain-size distribution along [100], but along the polarization vector ([001]) distribution narrows and shifts toward smaller sizes, thus implying that poling equalizes and decreases the coherent domain sizes. This may be caused by line defects (such as dislocations arranged in cells or low-angle boundaries) or extended defects (such as twins or stacking faults) that break up the ferroelectric domains in separate mutually incoherently diffracting domains, as evidenced by the [001] domain-size-distribution functions (compare Fig. 3), that is, along the poling-field vector. This is a direct indication that the inhomogeneous strains in Table I originate from real dislocations within domains. Moreover, the recent *in situ* x-ray-diffraction study of polycrystalline $BaTiO_3$ under a poling field up to 2 kV/mm noted that diffraction linewidths increased substantially under the electric field and decreased only after the field was switched off, which indicated that lattice distortion were relaxed, whereas the ratio of diffraction-line intensities did not change.[14] In the experiment, a substantial poling effect was achieved, as evidenced by relative Bragg diffraction intensities. Because this involves a massive 90° domain-wall removal and subsequent inhomogeneous strain relief, in the framework of a proposed theory of fictitious dislocation density,[25] diffraction lines were expected to gradually narrow with increasing field. This also indicates that electric field influences the defect concentration.



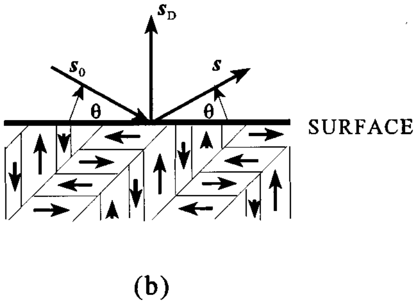


FIG. 4. Schematic representation of domain-configuration change upon poling. The c domain is defined by its polarization vector (along [001]) as perpendicular to the surface, and a domain has the polarization vector parallel to the surface of the specimen. The incident beam is along s_0, the diffracted beam is along s, and diffraction measurements are along the vector s_D. Bragg angle θ is measured from the specimen surface. (a) before poling, (b) after poling.

E. Dislocation density

Here we consider a relation between the diffraction-line broadening and crystal defects. Any disruption of the regular crystal lattice causes diffraction-line broadening. Although dislocations have the largest effect, both point and extended defects broaden and possibly shift diffraction lines.[31] We consider that the twinning in $BaTiO_3$, which is likely under the mechanical deformation, is suppressed under the external electric field. Furthermore, vacancies that can be produced by the movement of jogs created by dislocation intersection[35] are not expected to significantly contribute independently to the diffraction-line broadening because they are in turn attracted to the dislocation core.

The influence of dislocation fields on diffraction linewidths was studied by several authors.[36] The lattice strain energy per unit volume is

$$E_{\text{strain}}=CG\langle\epsilon^2\rangle. \tag{3}$$

The dislocation strain energy per unit length is[37]

$$E_{\text{dislocation}}=\frac{Gb^2}{4\pi z}\ln\frac{R}{r_0}. \tag{4}$$

Thus, the density of dislocations is estimated as

$$\rho_{\epsilon}=\frac{k}{F}\frac{\langle\epsilon^2\rangle}{b^2}. \tag{5}$$

Here $k=4\pi zC/\ln(R/r_0)$, $z=1$ for screw dislocations and $(1-\nu)$ for edge dislocations (ν is the Poisson ratio), C is a scaling constant in the range 4 (Ref. 36) to 15/2,[38] R and r_0 are outer and inner dislocation cutoff radii, and F is a correction factor that accounts for the mutual interaction energy of dislocations. The constant k can be calculated independently for simple cubic structures from geometrical considerations of dislocations.[39] For the pseudocubic $\{110\}\langle 110\rangle$ slip system reported for $BaTiO_3$,[26] we estimate $k\approx 19.4z$ and assume the Burgers vector $\boldsymbol{b}=a/2\,[110]$.

Similarly, if dislocations divide grains into coherent domains, such as faults and tilt (low-angle) boundaries[31] or cells,[40] the dislocation density can be estimated as[41]

$$\rho_D=n\frac{1}{\langle D\rangle_V}. \tag{6}$$

Here, $n=1$ for a random distribution of dislocations.[42] The parameters n and F are related: in the simplest case, if $\rho_D\approx\rho_{\epsilon}$ is obtained, it implies that one dislocation coincides with the edge of each cell, the dislocation separation and interaction is minimal, and $F=n=1$. The results in Table I show that consistently $\rho_D>\rho_{\epsilon}$. This implies that $F<1$, that is, dislocations decrease the strain energy by forming networks, such as small-angle or tilt boundaries (polygonization), where edge dislocations of the same sign form the boundary line, normal to the glide plane, that extends to the grain or domain boundary. The correct dislocation density is in between ρ_D and ρ_{ϵ}, of the order of $10^9/\mathrm{cm}^2$. We are not aware of any transmission-electron-microscopy study reporting dislocation density in $BaTiO_3$, but polygonization of edge dislocations was observed in many ionic crystals.[43]

The difference between ρ_D and ρ_{ϵ} is larger for the unpoled specimen where dislocation configuration may be relaxed maximally. Probably, dislocations are multiplied under the external poling field, which is visible by diffraction-line broadening observed by Valot *et al.*[14] After the poling field is switched off, the strain energy, which is increased by an average increase of domain size and accompanying increase of the homogeneous strain, is minimized by mutual annihilation and rearrangement of dislocations. In small-angle boundaries, dislocation long-range strain fields cancel at distances comparable to the dislocation separation distance within the boundary.[44] This decreases the dislocation strain energy by setting the outer cutoff dislocation radius R [see Eq. (4)], which is approximately equal to the grain or ferroelectric-domain size, to the interdislocation distance within a boundary. In effect, this alleviates a need for ferroelectric-domain creation in accord with Känzig[45] who identified the strain energy around defects as a major driving force for domain multiplication. We estimate the increase of inhomogeneous-strain energy upon poling from Eq. (3) and Table I to be about 20 $\mathrm{kJ/m^3}$. The increase in density of dislocations upon poling was confirmed by hardness measurements: It was found[46] that poling increased hardness parallel to the poling direction. This is consistent with the monotonic dependence of hardness on defect-related internal strains[47] and may indicate dislocation pileups. Pileups of edge dislocations against domain walls in $BaTiO_3$ were shown to be likely.[48] Another important consequence of dislocation rearrangement is possible microcrack formation by an energetically favorable reaction:[49]

$$a/2[0\bar{1}\bar{1}]+a/2[10\bar{1}]\rightarrow a/2[1\bar{1}\bar{0}]. \tag{7}$$

The pileups on $\{110\}$ planes could lead to crystal fracture, as calculated for MgO.[50]

IV. CONCLUSIONS

We show that dislocations play an important role in bulk microstructural changes that occur upon poling of polycrystalline $BaTiO_3$. Most of the domain switching involves a simple reversal in orientation, although there is an estimated 4–10% of 90° switching. Diffraction-line-broadening analysis shows large microstructural changes, especially along the direction of spontaneous-polarization and poling-field vector. The inhomogeneous strain upon poling is about the same order of magnitude as the strain caused by electrostriction during poling and indicates a substantial increase of the dislocation density. Dislocations are likely to form small-angle boundaries to relieve some of the internal stresses. However, the overall effect is the increase of inhomogeneous strain upon poling despite expectations for the opposite because of fewer 90° domain walls. The associated increase of internal stress influences the ferroelectric and phase-transition temperatures. Moreover, the increase of internal stress and defect concentration may have adverse consequences on both polycrystalline and epitaxial thin films through the accelerated degradation of dielectric properties. Because some dislocation reactions lead to microcracking, this may even result in the mechanical failure.

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[44] See Sprackling (Ref. 35) p. 79. Because in this simple model the dislocation separation within one boundary is equal to the separation between boundaries of the opposite sign, the dislocation strain field is practically constant throughout coherent domains. This implies that the strain-broadened diffraction-line profile is a Gauss function and the size-broadened profile is a Lorentz function, as was obtained for both [001] and [100] of the poled specimen. A more detailed discussion exceeds the scope of this paper. See, for instance, B. E. Warren, in *Progress in Metal Physics*, edited by B. Chalmers and R. King (Pergamon, New York, 1959), Vol. 8, p. 147 and Ref. 33, and M. Wilkens, J. Appl. Crystallogr. **12**, 119 (1979) for a criticism of Warren's approach.

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