Large Flexoelectriclike Response from the Spontaneously Polarized Surfaces in Ferroelectric Ceramics

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Nonpoled ferroelectric ceramics are thought to be nonpolar because of randomly oriented grains and the formation of ferroelectric domains in the grains. Here, we discover the surfaces (∼several μm thick) of ferroelectric ceramics are spontaneously polarized. Because the orientations of ferroelectric polarization of the opposite surfaces are antiparallel, ferroelectric ceramics are nonpolar as a whole. However, the ceramics exhibit a strong flexoelectriclike electromechanical response from the piezoelectric response of the polarized surfaces if they are asymmetrically strained (such as bending). Our results reveal a major mechanism to resolve one important but largely unresolved issue: the experimentally measured flexoelectric effect is typically orders of magnitude larger than the theoretically predicted value in ferroelectrics.

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Flexoelectricity is a universal electromechanical coupling effect in dielectrics whereby the electric polarization is generated by a strain gradient or mechanical stress generated by an electric field gradient [1–5]. A variety of intriguing applications, such as flexoelectric piezoelectric composites [6–9], mechanical-writing memory [10], and MEMS devices [11], have been explored by exploiting the effect. At the nanoscale, the effect can be intensified and significantly alters the dielectric properties [12], polarization orientation or polarity [13,14], and even mechanical properties of ferroelectrics [15]. For those flexoelectric-related applications and fundamental studies, the magnitude of the flexoelectric effect, which is characterized by the flexoelectric coefficient (μ_{ijkl}) or flexocoupling coefficient (f_{ijkl}, the ratio of μ_{ijkl} to the dielectric susceptibility), is a basic and necessary parameter. However, the experimentally measured f_{ijkl} of ferroelectric oxides often exceeds 100 V, several orders of magnitude higher than the theoretically predicted values (1–10 V) [2–4,16]. Furthermore, those measured coefficients are also substantially higher than the theoretical upper limit (typically <15 V) allowed by the stability of the crystal structures [2,3].

The reasons for the large discrepancy between the experimental and theoretical flexoelectric coefficients are not fully understood, although different mechanisms have been proposed. Surface piezoelectricity from the symmetry breaking of a material surface can generate a flexoelectric-like response, but typically, the f_{ijkl} is of the same order of magnitude as the intrinsic flexoelectric response of the crystal lattice [2,3,17]. Because most ferroelectric oxides are insulators, the recently proposed barrier-layer mechanism for the giant effective flexoelectric coefficient in semiconductive materials cannot be applicable to normal ferroelectrics [18]. The flexoelectric coefficient has also been found to be related to the inevitable chemical inhomogeneity produced during the high-temperature processing of ferroelectric oxides [19]; however, relatively consistent μ_{ijkl} measured in those oxides indicates the existence of other mechanisms because the coefficient of a material should depend strongly on the processing conditions based on this mechanism. Here, we show that the unexpectedly large flexoelectric coefficient measured in ferroelectric ceramics may mainly originate from a spontaneously polarized surface, which can be sustained well above the Curie temperature (T_c), and that the existence of this unique surface layer is a general phenomenon of different ferroelectric ceramic materials.

Barium titanate ($BaTiO_3$) ceramics were fabricated by the conventional solid reaction method [20]. The temperature dependence of the effective flexoelectric coefficient μ_ρ is presented in Fig. 1(a). The value of μ_ρ for all of the samples increases with temperature, reaches a maximum value at approximately 150 °C, and then decreases, following a similar variation trend to that of the dielectric constant [Fig. 1(b)]. A maximum μ_ρ of approximately 1000 $\mu C\,m^{-1}$ was measured in slowly cooled samples at ∼150 °C; this value is eight times larger than that of (Ba, Sr) TiO_3 ceramics, the materials with the highest flexoelectric coefficient of insulating ferroelectrics [4,23,24]. The large μ_ρ is not due to the barrier-layer mechanism because the $BaTiO_3$ ceramics are not semiconductive, as evidenced by the low dielectric loss in Fig. 1(b) [18]. The contribution of the charge trapped in defects to μ_ρ is also ruled out because the μ_ρ almost does not change after several consecutive

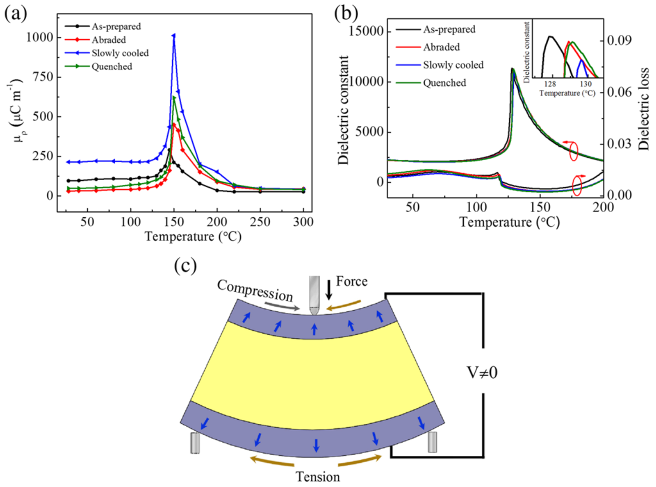

FIG. 1. The effective flexoelectric coefficient, dielectric properties of $BaTiO_3$ ceramics, and the effect of the polarized surfaces on the flexoelectric measurement. (a) The temperature dependence of μ_ρ. (b) The temperature dependence of the dielectric properties. The inset shows the dielectric constant near T_c. (c) A schematic drawing of the contribution of the spontaneously polarized surface to the measured μ_ρ under bending. An electric output is generated by a bending-induced piezoelectric response in the surface layer. The blue arrows indicate the orientation of the polarization in the surface.

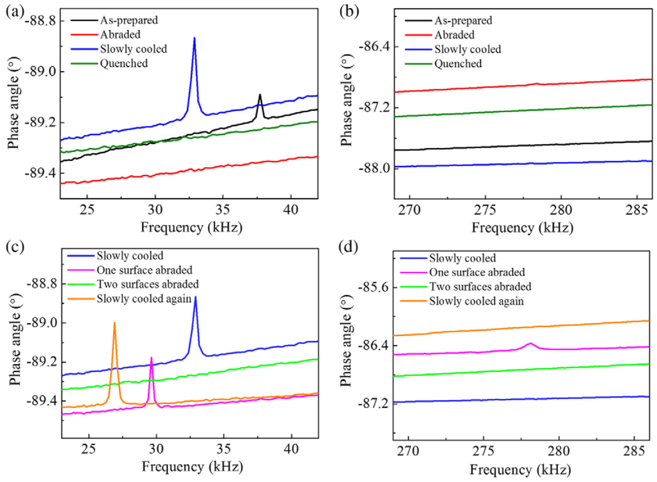

FIG. 2. Impedance phase angle curves of the nonpoled $BaTiO_3$ ceramic wafers near the resonance frequencies of the bending and radial vibration. (a),(b) The curves of the as-prepared, abraded, slowly cooled, and quenched samples. (c),(d) The curves of the slowly cooled samples and the samples after one surface or both surfaces were removed.

measurements of the temperature dependent μ_ρ (Fig. S1 of the Supplemental Material [20]) [17]. At room temperature, the μ_ρ of the as-prepared samples is approximately 120 $\mu\mathrm{C\,m^{-1}}$ (the equivalent flexocoupling coefficient $f_\rho > 6000$ V). After the ceramic wafers were abraded by 400-grit sandpaper (the abraded samples), the μ_ρ is significantly reduced to approximately 30 $\mu\mathrm{C\,m^{-1}}$. The μ_ρ is greatly enhanced to approximately 210 $\mu\mathrm{C\,m^{-1}}$ after the wafer was annealed at 200 °C for 30 min and then cooled naturally to room temperature (the slowly cooled samples); however, the μ_ρ is only approximately 45 $\mu\mathrm{C\,m^{-1}}$ after the wafer was quenched from 200 °C in a mixture of water and ice (the quenched samples). These results reveal that the measured μ_ρ of the as-prepared and slowly cooled $BaTiO_3$ ceramics is not intrinsic but originates primarily from a surface effect. The μ_ρ can also be significantly affected by the thermal history of the material.

In addition to the intrinsic response of crystal lattice, two surface mechanisms, the surface flexoelectricity and the surface piezoelectricity, may contribute to the measured flexoelectric response, but their response is either smaller than or comparable to the intrinsic response [2,3]. These mechanisms cannot explain the large flexoelectric response ($f_\rho > 6000$ V) measured in the as-prepared and slowly cooled samples. We speculate if the surfaces of $BaTiO_3$ ceramics possess the piezoelectric effect due to some reasons, similar to the surface piezoelectricity, the surfaces may generate a flexoelectriclike response. Because of the symmetrical shape of ceramic wafers, the piezoelectric response of the opposite surfaces should have different signs, and the ceramics do not exhibit a piezoelectric response as a whole when they are symmetrically pressed, as normally observed in nonpoled ferroelectric ceramics. If the ceramic wafers are asymmetrically stressed (such as bending), a flexoelectriclike polarization response can be generated from the piezoelectric surfaces, as schematically shown in Fig. 1(c).

To verify the existence of piezoelectric surfaces in the $BaTiO_3$ ceramics, the impedance spectra of the materials were measured. If the opposite surfaces have a piezoelectric response of different signs, a bending deformation of $BaTiO_3$ ceramic wafers can be generated under a uniform electric field, and at the mechanical resonance frequency, a change of electrical impedance should be detected. As presented in Fig. 2(a), impedance phase angle peaks near 35 kHz can be observed in the as-prepared and slowly cooled samples, which exhibit an enhanced flexoelectric-like response [Fig. 1(a)]. The peak frequencies were determined to be the bending resonance frequencies (f_b) of the ceramic wafers, which can be estimated by [25]

$$f_b \approx \frac{0.42h}{R^2}\sqrt{\frac{E}{\rho(1-\nu^2)}} \tag{1}$$

where R is the radius and h is the thickness of the ceramic wafer, E is the elastic modulus, ν is the Poisson's ratio, and ρ is the density of $BaTiO_3$ ceramics. For the slowly cooled samples, $h = 0.5$ mm, $R = 5.4$ mm, $\rho = 5.87\ \mathrm{g\,cm^{-3}}$, $\nu = 0.31$, and $E = 1.08 \times 10^{11}$ Pa [26]; the estimated f_b is 32.3 kHz, consistent with the measured value (32.9 kHz) shown in Fig. 2(a). For the abraded and quenched samples with a much smaller flexoelectriclike response, the resonance peak cannot be observed, indicating that the piezoelectric response becomes substantially weaker or even vanishes after the abrasion or quenching. Because the $BaTiO_3$ ceramics do not have a piezoelectric response as a whole, the resonance peaks typically observed in poled ceramics, such as those from the radial vibration of the ceramic wafers, should not be observed. As shown in Fig. 2(b), none of the samples exhibit the radial resonance peaks near 280 kHz, which can be estimated by [27]

$$f_r \approx \frac{2.05}{2\pi R}\sqrt{\frac{E}{\rho(1-\nu^2)}}. \tag{2}$$

For the slowly cooled samples, which exhibit the strongest surface effect, when only one surface was abraded, because of the piezoelectric effect of the opposite surface, the materials have a net piezoelectric response similar to that of poled ceramics. The piezoelectric response from the nonabraded surface can also cause the bending of the ceramic wafer under an electric field. Consequently, both resonance peaks from the bending and radial vibration can be observed in Figs. 2(c) and 2(d). After the removal of the two surfaces by abrasion, both peaks disappear, as expected. If the slow-cooling process was repeated on the abraded sample, the low-frequency resonance can be fully recovered, implying the recovery of the piezoelectric response in the surface. The measurement of the impedance spectra confirms the conjecture that there exist piezoelectric surfaces in nonpoled $BaTiO_3$ ceramics. Furthermore, the piezoelectric surfaces can be largely removed by abrasion or quenching and recovered by a slow-cooling process.

The existence of piezoelectric surface layers in $BaTiO_3$ ceramics was further corroborated by measuring the piezoelectric response of a slowly cooled ceramic wafer after the lower surface was abraded. A piezoelectric response ($\overline{d_{33}}$) of approximately $+1.5$–2.0 pC N^{-1}, which is from the upper piezoelectric surface, can be directly measured by a d_{33} meter. If the one-surface slowly cooled samples are treated as the composites of piezoelectric surface layers and nonpiezoelectric bulk, the relationship between $\overline{d_{33}}$ and the piezoelectric response of the surface layer (d_{33}^S) can be expressed as (see the Supplemental Material [20])

$$\overline{d_{33}} \approx d_{33}^S \frac{\varepsilon_2 t_1}{\varepsilon_1 t_2} \tag{3}$$

where ε_1 and ε_2 are the dielectric constants of the surface and the bulk and t_1 and t_2 are the thicknesses of the surface layer and the bulk.

Using the measured $\overline{d_{33}}$, the μ_ρ can be further estimated. The relationship between μ_ρ and the piezoelectric response of the surface layers can be expressed as (see the Supplemental Material [20])

$$\mu_\rho \approx \frac{2e_{31}^S \varepsilon_2 t_1}{\varepsilon_1} \tag{4}$$

where e_{31}^S is the piezoelectric stress coefficient of the surface layers. The surface layer is equivalent to a piezoelectric thin film clamped to a substrate (the bulk). The d_{33}^S and e_{31}^S can be expressed as [28,29]

$$d_{33}^S = d_{33} - \frac{2s_{13}^E}{s_{11}^E + s_{12}^E} d_{31} \tag{5}$$

and

$$e_{31}^S = \frac{d_{31}}{s_{11}^E + s_{12}^E} \tag{6}$$

where d_{33} and d_{31} are the piezoelectric strain coefficients of $BaTiO_3$ ceramics without constraint and s_{11}^E, s_{12}^E, and s_{13}^E are the elastic compliances. Using the data of poled $BaTiO_3$ ceramics, $s_{11}^E = 8.55 \times 10^{-12}$ m^2 N^{-1}, $s_{12}^E = -2.61 \times 10^{-12}$ m^2 N^{-1}, $s_{13}^E = -2.85 \times 10^{-12}$ m^{2}N^{-1}, and $d_{31}/d_{33} = -0.41$ [30]; based on Eqs. (3)–(6) and the measured $\overline{d_{33}}$, the estimated μ_ρ is 165–228 μC m^{-1} (see the Supplemental Material [20]), consistent with the measured value (~195 μC m^{-1}). This calculation illustrates that the measured μ_ρ of the slowly cooled $BaTiO_3$ ceramics is mainly from the piezoelectric response of the surfaces. According to Eq. (4), using the materials parameters of fully polarized $BaTiO_3$ ceramics [30] and assuming that the ε_1 and ε_2 are equal, the thickness of the surface layer is estimated to be approximately 7.5 μm (see the Supplemental Material [20]), which is reasonably consistent with our experimental observation. Experimentally, the μ_ρ was significantly reduced to a constant value after a layer of approximately 10 μm was abraded from the ceramic surfaces [Fig. 3(a)], and the thickness of the surface layer should be thinner than 10 μm.

Our experimental results and calculation unambiguously indicate that the surfaces in nonpoled $BaTiO_3$ ceramics are spontaneously polarized. Experimental results further reveal that the polarized surfaces in $BaTiO_3$ ceramics can be sustained well above T_c. As shown in Fig. 3(b), the bending resonance peaks from polarized surfaces can be observed at 180 °C, approximately 45 °C above T_c. It has been reported that the surfaces of some ferroelectric crystals may remain ferroelectric even above T_c [31–33] a phenomenon similar to the observation in $BaTiO_3$ ceramics. The high-temperature-stable ferroelectric surfaces were thought to originate from a compositional variation between the surface and bulk or from a strong electric field generated by the accumulation of defects or a ferroelectric-electrode interfacial Schottky barrier near the surfaces [31–33]. However, neither of the mechanisms can explain the polarized surface layer in $BaTiO_3$ ceramics. In the slowly cooled samples, which

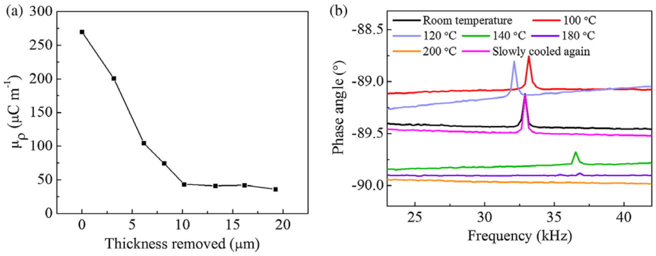

FIG. 3. The thickness and the temperature stability of the surface layer. (a) The dependence of the effective μ_ρ of the abraded and slowly cooled $BaTiO_3$ ceramic wafer on the thickness abraded from two opposite surfaces of the wafer. (b) The impedance spectra near the bending resonance frequency of a slowly cooled $BaTiO_3$ ceramic wafer measured at different temperatures.

exhibit the strongest flexoelectriclike response, the original surfaces were abraded off, and the composition of the new surfaces represents that of the bulk. Also, for the slowly cooled and quenched samples, the same surface can be reversibly converted from a piezoelectric state into a nonpiezoelectric (or weak piezoelectric) one by simply changing the cooling rate after a heat treatment at a low temperature (below 200 °C), and the mechanism of compositional variation cannot explain the observation. The ferroelectric-paraelectric phase transition of $BaTiO_3$ is of the first order. The ferroelectric phase can be induced from the paraelectric phase at a temperature above the T_c by an electric field, but the temperature should be below a limited temperature (~18 °C above the T_c) [34]. It is obvious that the polarized ferroelectric surface in $BaTiO_3$ ceramics cannot be induced at such a high temperature by an electric field, regardless of the origin of the field.

We propose that the observed polarized surface could be a stress-related phenomenon, as evidenced by the observation that the most significant enhancement of μ_ρ occurs after the ceramics are cooled from a temperature above T_c (~130 °C), as shown in Fig. 4(a). It is known that each grain in ferroelectric ceramics is constrained by the surrounding grains, and a residual stress can be produced due to the transition between ferroelectric and paraelectric phases [35]. The high-temperature processing of ceramics and mechanical abrasion may also cause a residual stress [36,37]. Unlike the grains in the bulk, which are constrained all around, those near the surface experience a biaxial strain. The biaxial strain can stabilize the ferroelectric phase and increases the T_c [38]. The existence of strain on the surfaces of the slowly cooled samples is supported by the x-ray diffraction (XRD) results shown in Figs. S6–S8 (see the Supplemental Material [20]). The (200)/(002) peaks were broadened near the surface, and the breadth was reduced after the surface was etched, indicating that an inhomogeneous strain exists near the surface. For the abraded samples, the inhomogeneous strain was estimated to be 0.15% based on the Williamson-Hall relation (Fig. S9 of the Supplemental Material [20]) [20,39]. The outmost surface was also found to have a structure with larger lattice parameters than the bulk, and an average strain approximately 0.3% can be estimated by the difference of the lattice parameter [20]. The maximum strain, which defines the temperature stability of the ferroelectric surface, is larger than these estimated strains [39]. Therefore, the strain near the surface of the slowly cooled samples could stabilize the ferroelectricity up to 180 °C [Fig. 3(b)] according to the correlation between T_c and the strain [38].

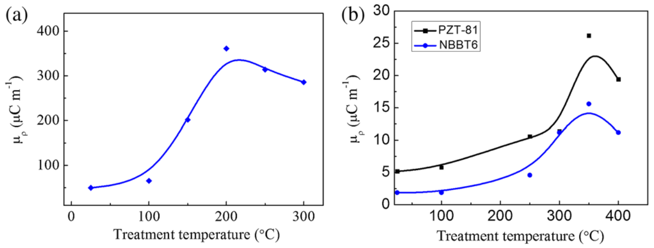

FIG. 4. The dependence of the effective μ_ρ on the heat treatment temperature in (a) $BaTiO_3$ ceramics and (b) $Pb(Zr,Ti)O_3$- and $Na_{1/2}Bi_{1/2}TiO_3$-based ceramics.

Because the grains are randomly oriented in ceramics, the ferroelectricity does not imply that the surface is polarized. For the slowly cooled $BaTiO_3$ ceramics, XRD results (Figs. S6–S8 of the Supplemental Material [20]) reveal that the strain near the surface varies with the depth from the surface, and a strain gradient can be developed. The resulting flexoelectric effect may polarize the ferroelectric surface [2,3,10]. In the abraded and slowly cooled $BaTiO_3$, the strain gradient is estimated to be approximately 150 m^{-1} using the estimated inhomogeneous strain (0.15%) and the thickness of the surface layer (~10 μm). For the abraded samples, the contribution of the surface effect to the measured flexoelectric effect was largely eliminated. The f_ρ of the abraded samples, which can be obtained from the dielectric properties and the μ_ρ, is approximately 2000 V at room temperature. Apparently, the large f_ρ should also mainly originate from some extrinsic mechanisms [2,3]. Nevertheless, these extrinsic mechanisms behave similarly to the intrinsic effect. With f_ρ and the estimated strain gradient, the equivalent electric field from the flexoelectriclike response is estimated to be approximately 0.3 MV m^{-1} (the product of f_ρ and the strain gradient), which is larger than E_c (~0.2 MV m^{-1}, Fig. S2 of the Supplemental Material [20]) and strong enough to polarize the surface layer. In addition, because the $BaTiO_3$ ceramics were slowly cooled from a temperature above T_c, the orientation of the polarization is significantly easier.

For the quenched samples, when the temperature is quickly decreased from a temperature above T_c, thermal stress can be generated near the surface. As a result, similar to the bulk, the grains near the surface experience three-dimensional stress during the cooling process and the stress relaxation is impeded. XRD results suggest that the structure of the surface of the nonabraded and quenched sample is almost the same as that of the bulk (Fig. S6 of the Supplemental Material [20]), and hence no or much less strain gradient exists near the surface. Consequently, the surface is not or weakly polarized. Experimentally, a significantly smaller effective flexoelectric response was measured in quenched samples.

It should be noted that the mechanism of the spontaneously polarized surface layer presented here is different from the theoretically predicted surface piezoelectricity. The surface piezoelectricity originates from the symmetry breaking of the surface, and typically the piezoelectric response is from an atomically thin layer (in the angstrom range) [2,3,40]. The piezoelectric response of the surface of $BaTiO_3$ ceramics discussed here is from the alignment of ferroelectric polarization, and the surface layer is significantly thicker (several μm). The piezoelectric response of the polarized ferroelectric surface is also substantially higher than that of the surface piezoelectricity.

The occurrence of spontaneously polarized surfaces is also a general phenomenon in different ferroelectric ceramics. In $Pb(Zr, Ti)O_3$ (PZT)- and $Na_{1/2}Bi_{1/2}TiO_3$-based ceramics, an enhancement of μ_ρ after the materials were slowly cooled from a treatment temperature above T_c can also be observed, the mechanism of which should be the same as that of $BaTiO_3$. The dependence of effective μ_ρ of the abraded commercial PZT-81 ceramics ($T_c \sim 300\,^\circ\mathrm{C}$) and $0.94Na_{1/2}Bi_{1/2}TiO_3 - 0.06BaTiO_3$ (NBBT6) ceramics (the dielectric maximum temperature $T_m \sim 300\,^\circ\mathrm{C}$) on the treatment temperatures is shown in Fig. 4(b). It is clear that the effective μ_ρ can be enhanced by cooling slowly from a temperature above T_c or T_m.

In this Letter, we reveal the existence of high-temperature-stable spontaneously polarized surface layers in $BaTiO_3$ ferroelectric ceramics. The polarized surface, which can generate a strong flexoelectriclike response, is a major mechanism for the unexpectedly large experimental flexoelectric coefficients in ferroelectrics. We also show that the unusual surface effect is a general phenomenon in different ferroelectric ceramics. The discovery of the spontaneously polarized surface is not only important for the understanding of mechanisms of the flexoelectricity in ferroelectrics, the large flexoelectriclike response from the surface effect can also be exploited to design new electromechanical materials or devices with improved performance, such as flexoelectric piezoelectric composites [6–9]. Our work also presents a new perspective to understand the surface of ferroelectrics, which has a significant effect on the physical properties of ferroelectric materials, especially for the materials at a small scale (the size effect) [41]. Although the materials investigated here are relatively thick and the effect is difficult to discern, we indeed observed that the slowly cooled samples have different dielectric properties from the abraded or quenched samples near T_c [Fig. 1(b)] and different polarization hysteresis behaviors under a high field (Fig. S2 of the Supplemental Material [20]). It can be expected that when the thickness is reduced to a value comparable to that of the spontaneously polarized surface layer, the effect may become more significant.

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