

Effects of residual stress caused by abrasion on the flexoelectric response of BaTiO₃ ceramics

Xu Yang¹, Dongxia Tian¹, Xiaoyan Zhang¹, Ruzhong Zuo², and Baojin Chu¹ ✉

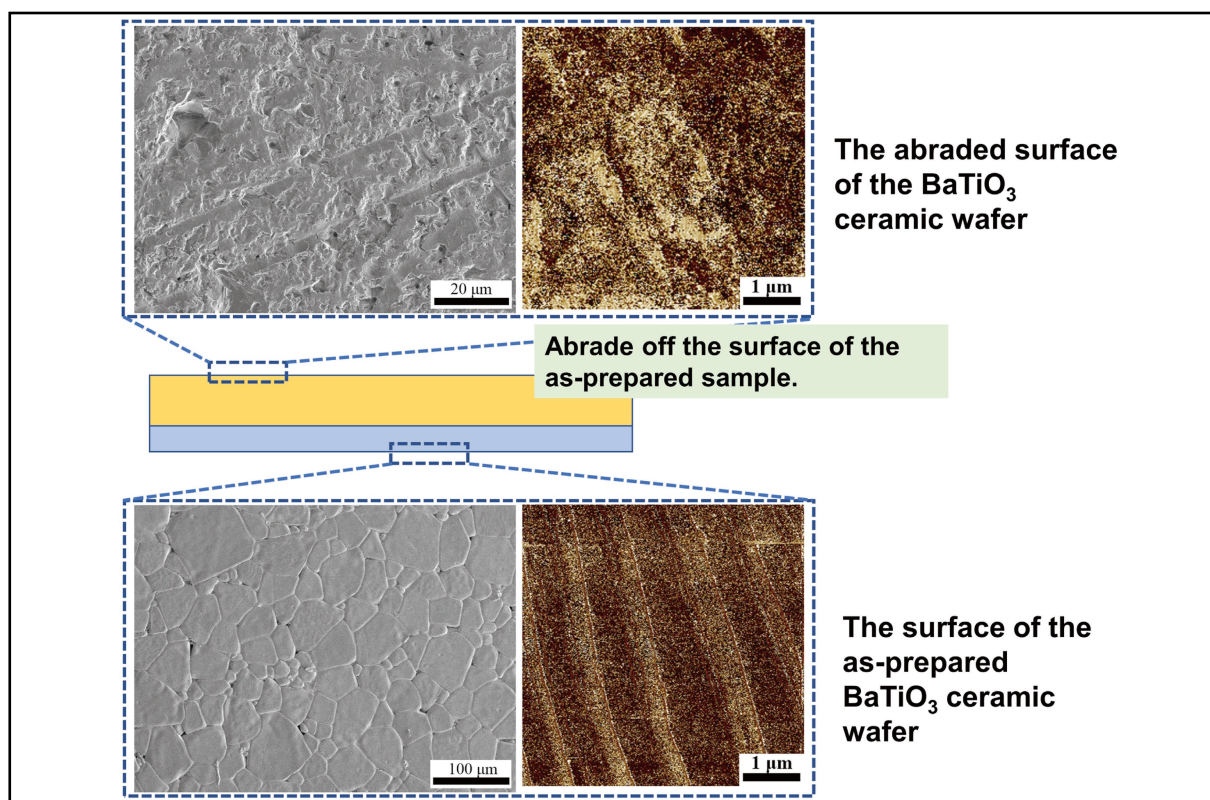
¹CAS Key Laboratory of Materials for Energy Conversion and Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, China;

²Anhui Key Laboratory of High-performance Non-ferrous Metal Materials, School of Materials Science and Engineering, Anhui Polytechnic University, Wuhu 241000, China

✉Correspondence: Baojin Chu, E-mail: chubj@ustc.edu.cn

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Graphical abstract



Although abrasion will cause damage to the BaTiO₃ ceramic surface and introduce stress, this stress is not the primary factor in the development of polarized surface layers.

Public summary

- The effect of residual stress introduced by abrasion on the formation of polarized surface layers of BaTiO₃ is discussed.
- The stress caused by mechanical abrasion only has a slight effect on the flexoelectric coefficient of BaTiO₃ ceramics.
- The stress caused by the phase transition and the constraint from neighboring grains in the ceramics are the main reasons for the formation of polarized surface layers.

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²Anhui Key Laboratory of High-performance Non-ferrous Metal Materials, School of Materials Science and Engineering, Anhui Polytechnic University, Wuhu 241000, China

✉ Correspondence: Baojin Chu, E-mail: chubj@ustc.edu.cn

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Abstract: The spontaneously polarized surface layer, which originates from stress relaxation, has been proposed for the unexpectedly large flexoelectric response measured in ferroelectric ceramics. However, the source of the stress that led to the polarized surface layer is still not completely known. In this work, the effect of surface stress on the microstructure, dielectric properties and flexoelectric response of BaTiO₃ ceramics abraded by abrasive papers of various grit sizes was systematically studied. Compared with the as-prepared sample, the flexoelectric coefficients of abraded BaTiO₃ ceramics decreased from ~600 $\mu\text{C}/\text{m}$ to less than 200 $\mu\text{C}/\text{m}$. The flexoelectric coefficients of all the samples, however, recovered to ~500 $\mu\text{C}/\text{m}$ following heat treatment at 200 °C and a subsequent slow cooling process. The results indicate that abrasion can introduce stress on the surface layers and affect the flexoelectric response of ferroelectric ceramics to some extent, but the stress is not the main reason for the formation of polarized surface layers.

Keywords: ferroelectric ceramics; flexoelectricity; abrasion; surface layer

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1 Introduction

Flexoelectricity is a universal electromechanical coupling effect in solid dielectrics, which describes the interaction between dielectric polarization and strain gradient^[1–4]. Unlike the piezoelectric effect, which only appears in materials without a center of symmetry, the flexoelectric effect has no restriction on the crystal structure of dielectric materials, a feature promising for device applications^[5–7]. The magnitude of the flexoelectric effect is characterized by the flexoelectric coefficient (μ_{ijkl}) or flexocoupling coefficient (f_{ijkl}). μ_{ijkl} of simple low-permittivity dielectrics is theoretically estimated to be on the order of 10^{-11} – 10^{-10} C/m^[8,9]. It was not until the beginning of the 2000 s that Ma and Cross discovered that ferroelectric ceramics had very large flexoelectric coefficients, which are several orders of magnitude larger than the theoretical values. The findings arouse considerable interest in the flexoelectric effect of ferroelectric materials^[4–6,10–13].

Different mechanisms have been proposed for the large deviation of experimental flexoelectric coefficients from the theoretical values. For example, the inhomogeneous deformation of nanodomains or nanopolar regions in relaxor ferroelectrics results in a preferred orientation, which enhances the flexoelectric response^[11]. Our recent study revealed that the large flexoelectric coefficient of ferroelectric ceramics is mainly from spontaneously polarized surfaces^[14]. The formation of polarized surfaces is a stress-related phenomenon that is greatly affected by the thermal history. However, the

origin of the residual stress has not been fully explored. One source of the stress (the internal stress, the stress generated within the sample during or after sample preparation without external interaction, including the stress generated during phase transition) was thought to originate from the phase transition that occurs when the ceramics are cooled from a high temperature and the constraint from neighboring grains in the ceramics. BaTiO₃ (BT) ceramics undergo a cubic-tetragonal phase transition when slowly cooled from a temperature (200 °C) higher than the Curie temperature. The surface grains are subjected to biaxial stress and are not constrained in the direction perpendicular to the surface. The bulk grains, however, are constrained in all directions. When the ceramics are cooled down slowly from the temperature, the stress produced from the phase transition can be partly relaxed in the thickness direction in the surface grains, creating a strain gradient. The resulting flexoelectric effect may polarize the ferroelectric surface. On the other hand, sintered ferroelectric ceramics are often subjected to abrasion to obtain targeted thicknesses before various physical measurements. Mechanical abrasion can introduce extra residual stress (the external stress, the stress in the material caused by the interaction between the post-treatment process and the sample after the sample has been prepared, including the abrasion stress) and affect the structure and properties of the ceramic surface^[15–17]. It has been reported that abrasion causes the preferred orientation of ferroelectric domains in surface layers^[15,16]. The properties of the abraded surface layer were

also believed to be distinct from those of the bulk. However, considering that abrasion can affect a thickness of several tens of micrometers, which coincides with the thickness of the observed polarized surface layer, it makes sense to investigate whether internal or external stress predominates in the formation of the polar surface layer. To address this issue, here, the flexoelectric coefficients of BT ceramics abraded by abrasive papers with different grit sizes were systematically investigated. Using abrasive papers of different grit sizes leads to varied residual mechanical stress, but our results suggest that the abrasion-induced stress only has a slight impact on the measured flexoelectric coefficients. Therefore, it is not the main reason for the formation of polar surface layers.

2 Materials and methods

The conventional solid-state reaction method was used to fabricate BT ceramics. BaCO₃ (purity ≥99.0%, Aladdin Biochemical Technology Co., Ltd., Shanghai, China) and TiO₂ (purity ≥99.0%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) were weighed according to the stoichiometric ratio and ball-milled in ethanol for 12 h. After drying, the mixture was calcined at 1200 °C for 2 h. The calcined powder was crushed in a mortar and then ball-milled again. Polyvinyl alcohol (PVA) was added to the powder as a binder. The powder was then pressed into ceramic wafers (half an inch in diameter) in a steel die. After the binder was burned out at 800 °C for 2 h, the green bodies were sintered at 1300 °C for 2 h in air (the as-prepared samples). The BT ceramics were mechanically abraded to a thickness of 0.5 mm with 240-grit (particle size 60 μm), 400-grit (particle size 38 μm), 1500-grit (particle size 12 μm) or 5000-grit (particle size 2.7 μm) silicon carbide abrasive papers (the abraded samples). The abraded ceramics were heat treated at a temperature (200 °C) higher than their Curie temperature for 0.5 h and then cooled slowly in an oven (the slowly cooled samples).

The crystal structures of the abraded samples were characterized by X-ray diffraction using a Rigaku Smartlab diffractometer (Rigaku, Tokyo, Japan). The microstructure characterization of the abraded samples was performed using a scanning electron microscope (GeminiSEM 500, Carl Zeiss, Oberkochen, Germany). Before electrical and dielectric measurements, the surfaces of ceramic wafers were sputtered with a gold electrode by a DC sputtering method in a sputter coater (Emitech Q150T, Electron Microscopy Sciences, Hatfield, PA, USA). The temperature-dependent dielectric properties of the wafers were measured at a heating rate of 2 °C/min by an automatic test system, including a computer, a furnace, and an E4980 LCR meter (Agilent Technology, Santa Clara, CA, USA). The polarization vs. electric field (P–E) hysteresis loop curves were measured using a modified Sawyer-Tower circuit (Polyktech, State College, USA) at room temperature. Domain structures and polarization states were characterized by piezoresponse force microscopy (PFM) (Dimension Icon, Bruker, USA). A Pt/Ir-coated silicon cantilever with a spring constant of 3 N/m and a resonance frequency of 75 kHz was used for domain imaging in PFM by applying a 7.2 kHz, 4.5 V_{ac} voltage. The effective piezoelectric response d_{33} caused by the flexoelectric effect was measured by a “point-ring”

method using a quasistatic d_{33} meter (ZJ-3AN, Institute of Acoustics, CAS, Beijing, China), as reported in our prior study^[18]. The flexoelectric coefficient μ_p can be expressed as

$$\mu_p = \frac{2Eh^3d_{33}}{3(1-\sigma)^2R^2}, \quad (1)$$

where E is the elastic modulus of the samples; h is the thickness of the wafer; σ is Poisson's ratio; and R is the radius of the wafer.

3 Results and discussion

The XRD patterns of the BT ceramics with different abrasion conditions are shown in Fig. 1a. Abrasion does not change the crystal structure of the ceramics. All the samples have a tetragonal perovskite structure, and no obvious secondary phases can be observed. However, after abrasion, the intensity ratio of the (002)/(200) peaks R_a substantially changes, indicating that the orientation of the 90° domain has been induced by the abrasion^[15,16], as shown in the right panel of Fig. 1a. Fig. 1b–f shows the Rietveld refinement results of the XRD patterns. The dependence of the ratio on the particle sizes of the abrasive papers is summarized in Fig. 1g. The R_a value of the as-prepared sample is 0.59. With increasing abrasive paper particle size, the ratio increases obviously and approaches 3.12 after abrading the ceramic with 240-grit abrasive paper. The orientation effect can be attributed to the stress exerted on the ceramic surface during the abrasion process^[16,19,20].

The surface SEM images of the as-prepared and abraded samples are presented in Fig. 2a–d. The grain size of the ceramics is in the range of ~20 μm–100 μm (Fig. 2a). As the particle size of abrasive paper increases, the ceramic surfaces become rougher, and scratches can be observed on the surfaces. Therefore, mechanical abrasion causes significant damage to the surfaces of ceramics.

Fig. 3a shows the temperature dependences of the weak-field dielectric constant and loss (measurement frequency 1 kHz) of BT ceramics after abrasion and heat treatment at 200 °C. Compared with the as-prepared sample, a slight change in the dielectric properties can be discernible after abrasion and heat treatment. The dielectric constants of those samples close to room temperature (30 °C) and the Curie temperature (T_C , 133 °C) are summarized in Fig. 3b and c. At room temperature, the dielectric constant of the abraded samples is slightly higher than that of the as-prepared samples, and no significant difference exists among the samples abraded by abrasive papers with different grit sizes. Similarly, at 133 °C, the dielectric constants of the abraded samples are similar but smaller than that of the as-prepared sample. Since the abrasion only affects the surface regions of the ceramics, the observed change in the dielectric constant following abrasion suggests that the surface layers formed by the abrasion have a significant impact on the dielectric property of the whole ceramic samples. The increase and decrease in the dielectric constant at 30 °C and 133 °C after abrasion could be related to the effect of abrasion stress on the phase transitions (orthogonal-tetragonal and tetragonal-cubic phase transitions) in the surface layer around the temperatures^[21]. From Fig. 3b and c, we can see that after the heat treatment at 200 °C, the

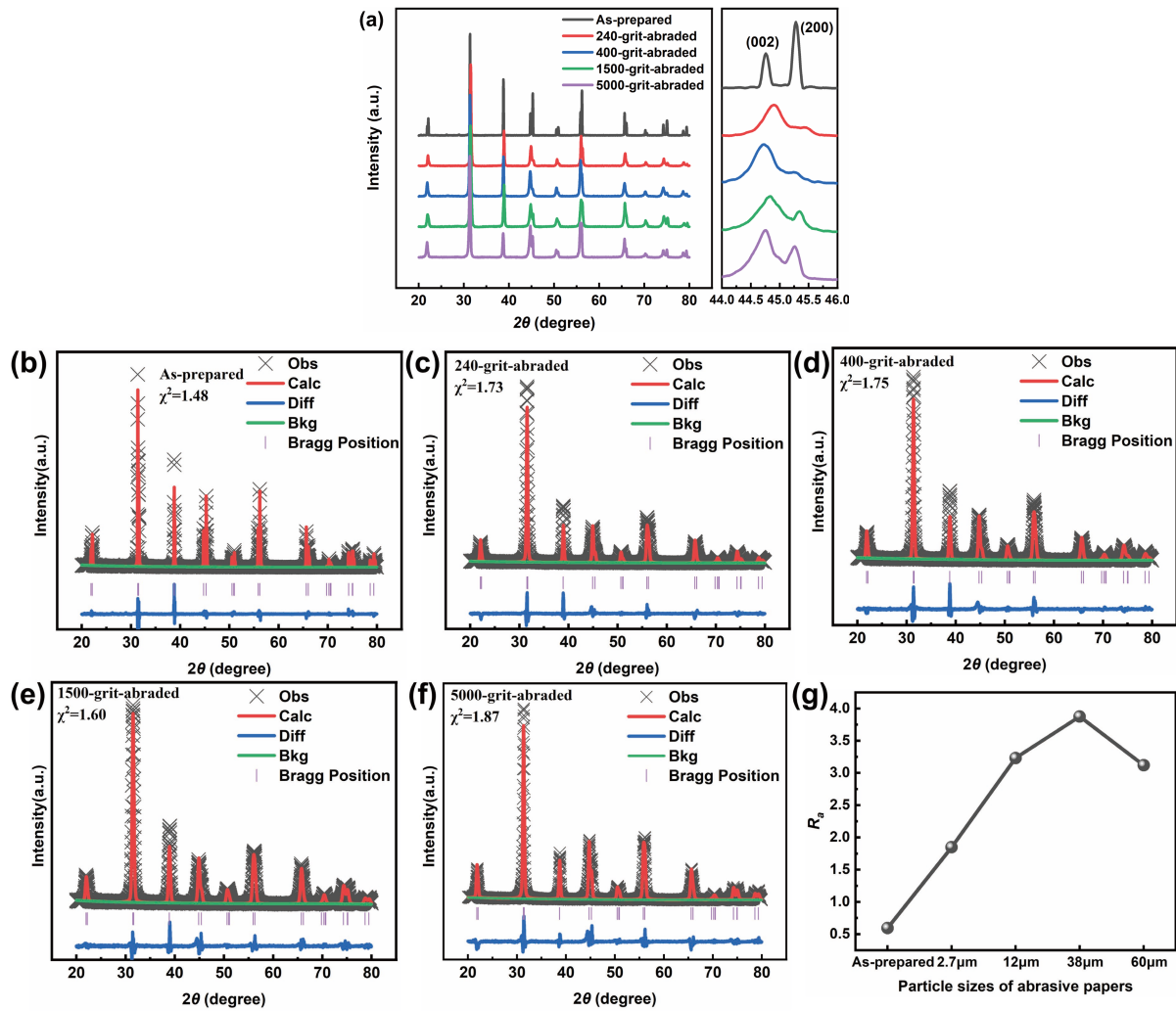


Fig. 1. (a) The XRD patterns of BT ceramics abraded with different abrasive papers. (b–f) Analysis of the XRD patterns shown in (a) using the Rietveld refinement method. “×” marks represent the diffraction peaks, and the red solid lines are fitted curves. The difference between the experimental results and fitted curve is shown as blue curves. (g) The intensity ratio of (002)/(200) peaks R_a of BT ceramics abraded with abrasive papers of different particle sizes.

dielectric constants of the samples at approximately room temperature and T_C increase. As discussed in our prior study, after heat treatment at 200 °C, the stress near the surface of the ceramics could be relaxed, leading to the formation of spontaneously polarized surface layers^[14]. Stress relaxation may repair the damage caused by abrasion and improve the dielectric property of the surface layers. The impact of the abrasion and heat treatment on the dielectric property of the ceramics is consistent with our prior conclusion that the surface layers might play an important role in the physical properties of ferroelectric ceramics when the thickness of the ceramics is thinner than 1 mm^[21].

The effect of abrasion and heat treatment at 200 °C on the ferroelectric hysteresis loops was also investigated, as illustrated in Fig. 4a and b. The coercive field E_c and maximum polarization P_{max} of those samples are summarized in Fig. 4c and d. As shown in Fig. 4c, abrasion slightly increases E_c , but the grit sizes of the abrasive papers have a less significant effect on E_c . Because abrasion generates damage and defects, such as dislocations, on the surface regions of the ceramics, and sometimes the surface layers are thought to become non-

ferroelectric, it is understandable that the surface layers of the abraded ceramics have a larger E_c , increasing in the E_c of the abraded ceramics^[17,22]. After the heat treatment at 200 °C, the E_c of the abraded ceramics can be further increased. As reported in a prior study, the heat treatment and subsequent slow cooling of ferroelectric ceramics produce polarized surface layers because of the inhomogeneous stress and flexoelectric effect near the surface regions^[14]. The increase in E_c of the heat-treated ceramics can be attributed to the polarized surface layers. Because of the flexoelectric effect-induced internal field, the layers may have a larger E_c than the ceramics before heat treatment. For the as-prepared samples, E_c almost does not change before and after the heat treatment because after sintering, the samples were cooled from a high temperature, which can be thought of as a heat treatment. The maximum polarization P_{max} (under an electric field of 3 kV/mm) of the abraded samples is slightly lower than that of the as-prepared samples, suggesting the effect of the change in the surface layers on the polarization response of BaTiO₃ ceramics, as shown in Fig. 4d.

The measurement of dielectric properties indicates the

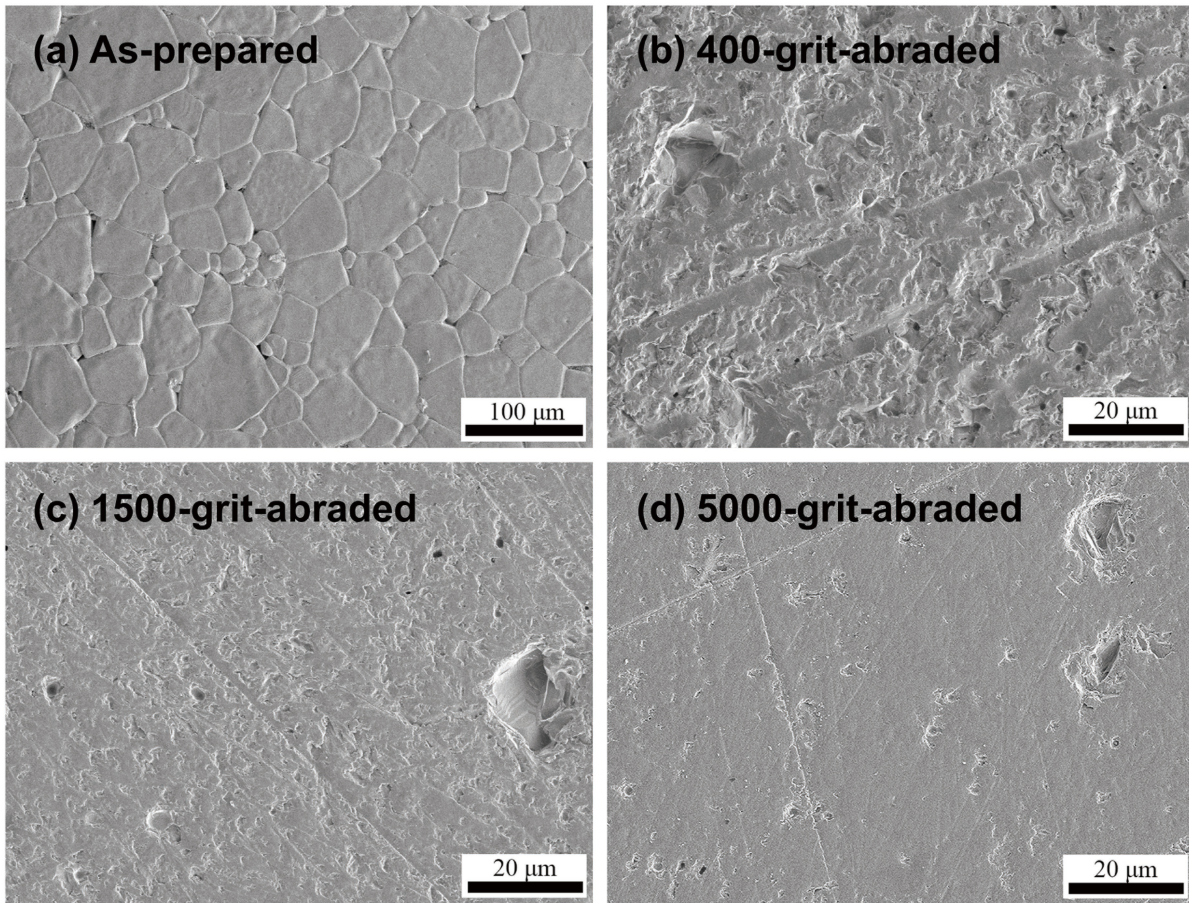


Fig. 2. SEM images of BT ceramics: (a) as-prepared, (b) 400-grit-abraded, (c) 1500-grit-abraded, (d) 5000-grit-abraded.

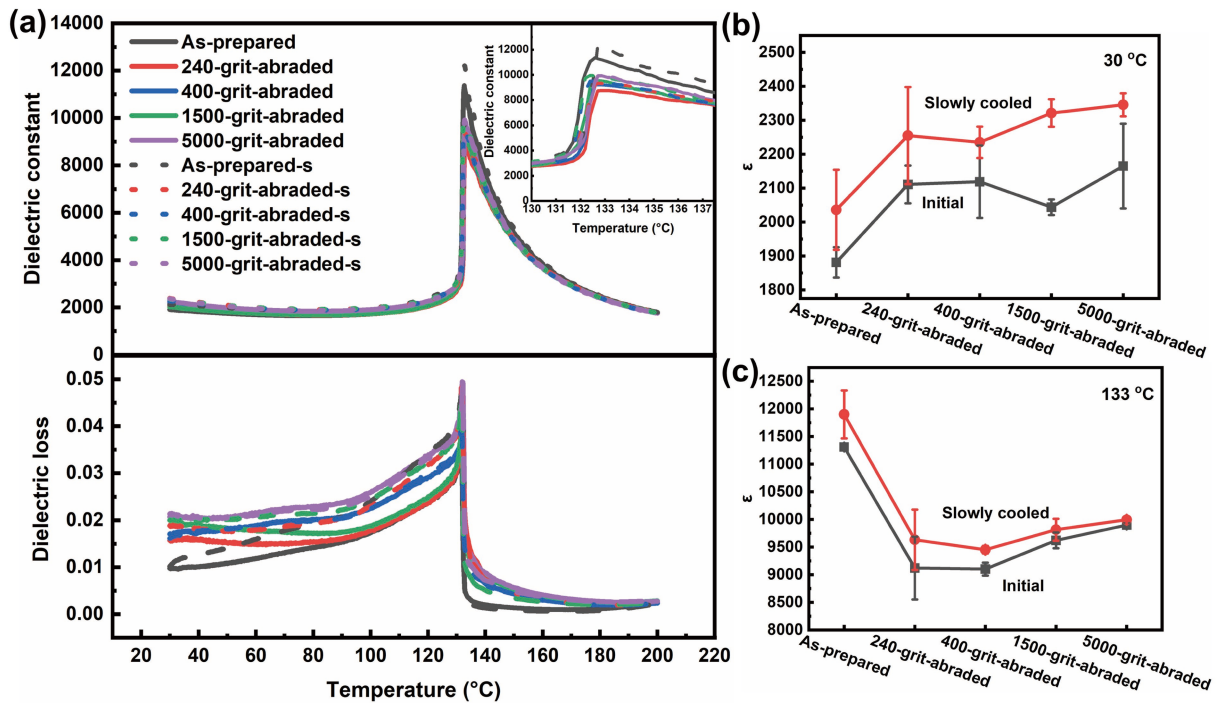


Fig. 3. (a) The temperature dependence of the dielectric constant and loss of as-prepared and abraded BT ceramics before and after heat treatment at 1 kHz. The inset shows the dielectric constant near T_C . (b, c) The dielectric constant of BT ceramics before and after heat treatment with different abrasion conditions at 30 °C and 133 °C, respectively.

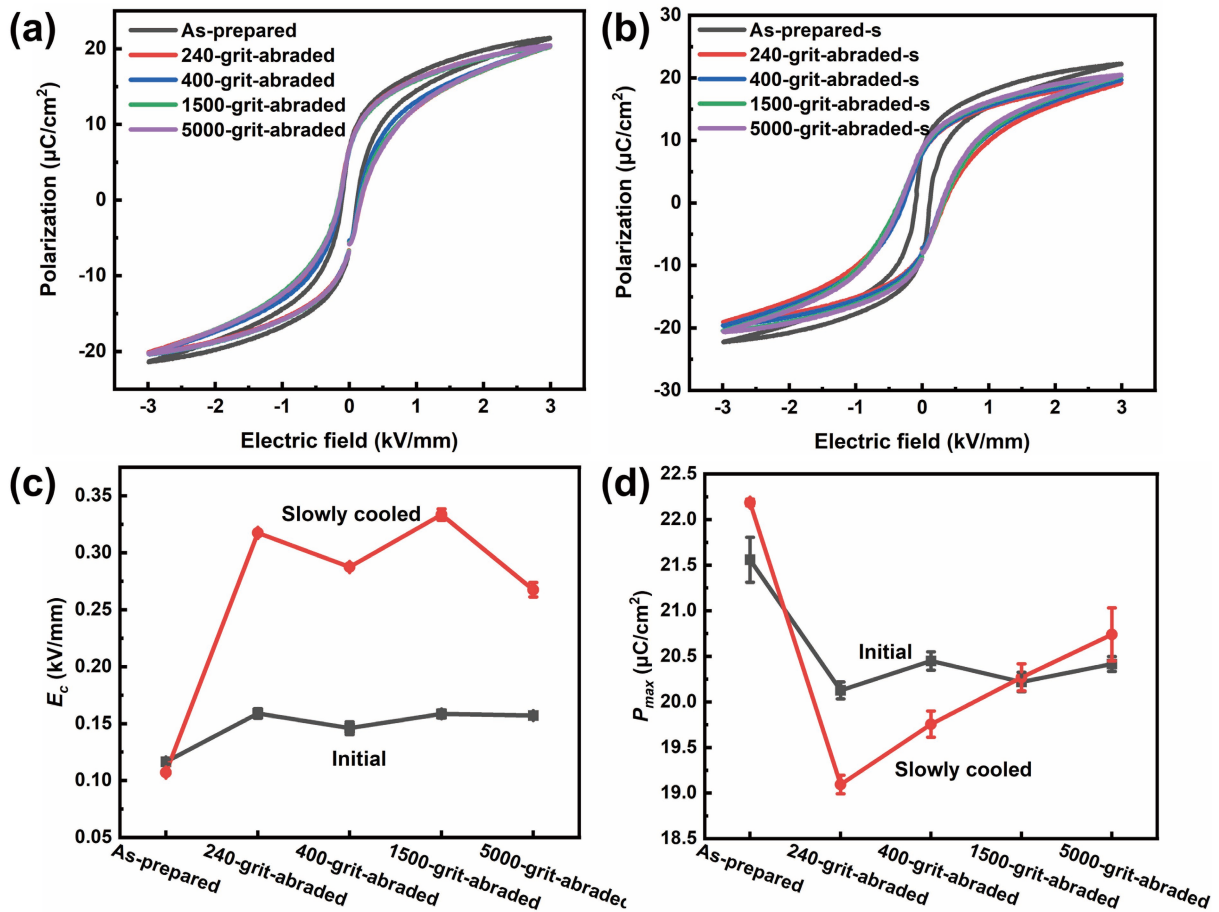


Fig. 4. (a, b) The P-E hysteresis loops of as-prepared and abraded BT ceramics (measured at room temperature) before and after the heat treatment at 200 °C, respectively. (c) Dependence of coercive field E_c of BT ceramics on the grit size of the abrasive paper. (d) Dependence of maximum polarization P_{max} of BT ceramics on the grit size of the abrasive paper.

existence of surface layers and the important influence of the layers on the dielectric properties. Because large stress is generated on the surface of the ceramics during abrasion and the spontaneously polarized surface layers, the key mechanism for the flexoelectric response measured in the ferroelectrics is the result of the stress relaxation near surface regions. Is it the stress generated by the abrasion that causes polarized surface layers^[14]? To investigate the effect of the abrasion-induced stress on the flexoelectric response of BaTiO₃, the flexoelectric coefficient μ_p was obtained using the measured apparent d_{33} and Eq. (1). Fig. 5 shows the μ_p of the BT ceramics before and after abrasion or heat treatment. After abrasion, μ_p is significantly reduced from ~600 $\mu\text{C}/\text{m}$ to less than 200 $\mu\text{C}/\text{m}$ owing to the removal of polarized surface layers formed on the as-prepared samples. We also notice that for the samples abraded with abrasive papers of a smaller particle size, μ_p is larger compared with that measured in the sample abraded with a 60 μm particle size. This can be explained by less damage caused by the abrasive papers with smaller particle sizes. After the heat treatment at 200 °C, by which the stress in ceramics can be relaxed to generate polarized surfaces, the μ_p of the abraded samples can be recovered to a value close to that of the as-prepared samples. This result suggests that the stress generated by abrasion should not be the main source of stress leading to the polarized surface layers. On the other

hand, as shown in Fig. 5, the small decline in μ_p with the reduction in particle sizes of the abrasive papers indicates that the stress caused by the abrasion may affect the formation of the polarized surface layers to some extent. In addition, all the samples that we measured exhibit piezoelectric responses of the same sign. This implies that the flexoelectric response caused by the abrasion stress should have the same sign as the

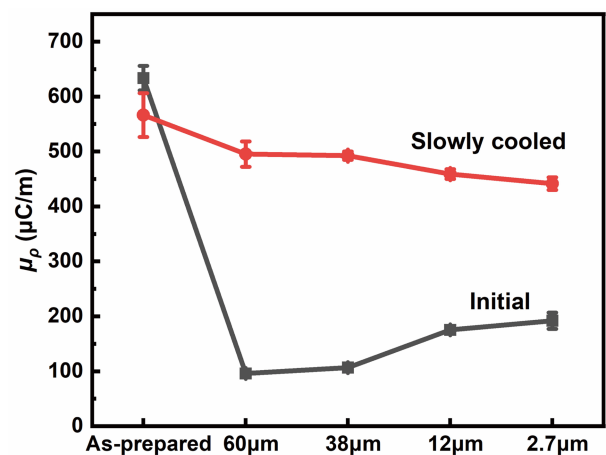


Fig. 5. The dependence of the flexoelectric coefficient μ_p of BT ceramics on the particle size of the abrasive paper at room temperature.

response caused by the stress during the phase transition. Therefore, our experimental results support the conclusion that the stress caused by mechanical abrasion has a slight effect on the measured flexoelectric response.

The temperature dependence of the flexoelectric coefficient μ_p of the as-prepared and abraded BT ceramics was further investigated, as shown in Fig. 6. The value of μ_p for all samples remains essentially unchanged as the temperature rises. When the temperature reaches 130 °C, μ_p starts to increase, reaches a maximum value at approximately 160 °C, and then falls rapidly, following a variation trend similar to that of the dielectric constant shown in Fig. 3a. μ_p has a

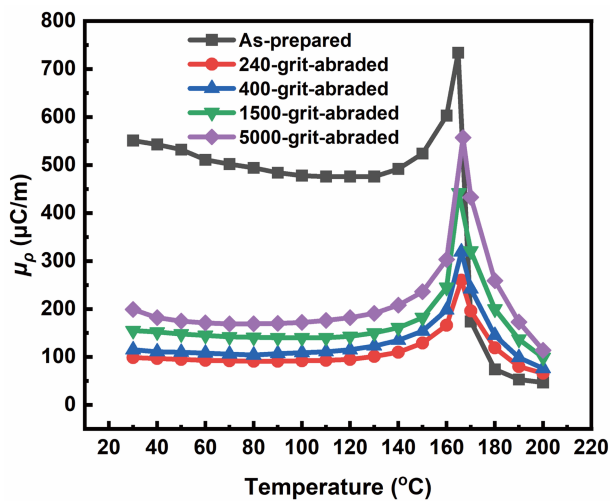


Fig. 6. Temperature dependence of the flexoelectric coefficient μ_p of the as-prepared and abraded BT ceramics.

larger value near T_C and decreases when the temperature deviates from T_C . Moreover, the decrease in μ_p is more obvious above T_C than below T_C . This can be attributed to the fact that the polarized surface layer is the main contributor to the flexoelectric response when the temperature is below T_C , and it gradually disappears when the temperature is above T_C .

To further investigate the surface domain structures and polarization states of BT ceramics, piezoresponse force microscopy (PFM) analysis was used to characterize surface domains and polarization states^[23–25]. From the out-of-plane PFM phase images of the as-prepared samples before and after a heat treatment above T_C , as shown in Fig. 7a and b, we observe two types of domains, and the analysis of the distribution of the number of polarization orientations is shown in Fig. 7c^[26–28]. There are mainly two orientations, namely, $\sim -70^\circ$ and $\sim 170^\circ$ for the as-prepared samples before heat treatment and $\sim -110^\circ$ and $\sim 140^\circ$ for the samples after heat treatment. The phase difference of the two states is approximately -270° , suggesting that 90° domains are formed. After the sample was abraded with 5000-grit abrasive paper, the stripe-shaped domain structure on the surface could not be observed, as shown in Fig. 7d and e. The analysis of the polarization orientation is shown in Fig. 7f. There are also two main polarization orientations in the abraded ceramics before and after the heat treatment above T_C , that is, $\sim -70^\circ$ and $\sim 109^\circ$. The phase difference between the two orientations is approximately 180° , indicating that 180° domains are formed. Fig. 7c and f also shows that for the as-prepared samples and the abraded ceramic after the heat treatment, there are preferable polarization orientations. This observation is consistent with the existence of polarized surface layers in these samples. The PFM results are also consistent with the above

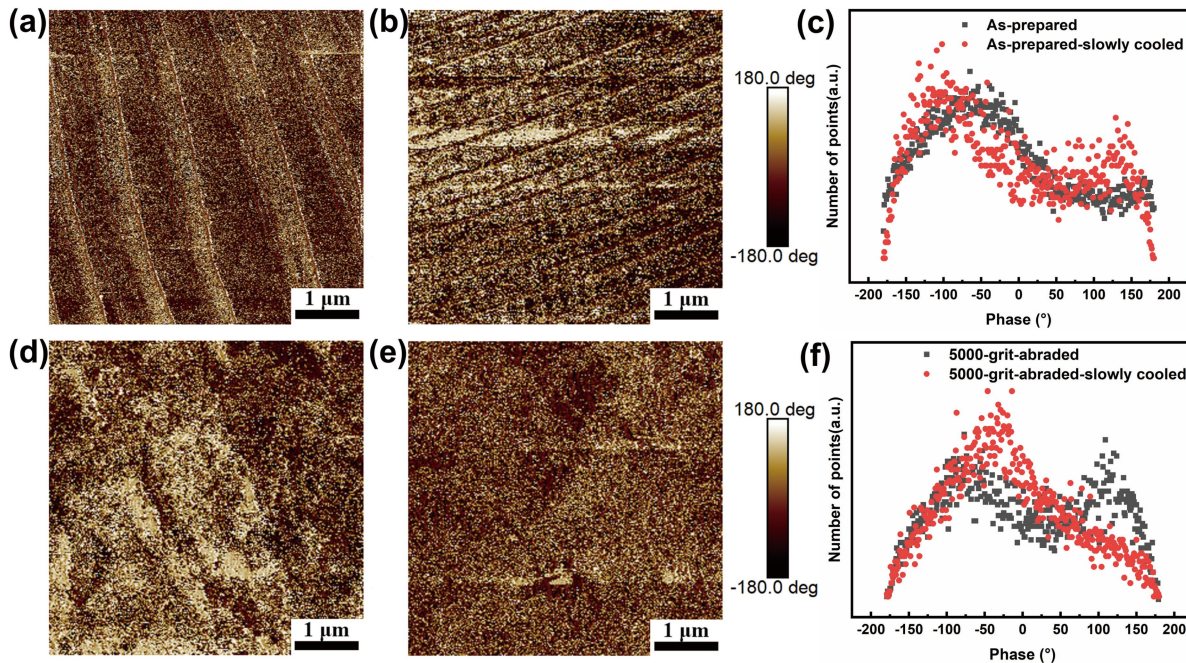


Fig. 7. PFM images of BT ceramics. (a) Phase contrast PFM images before heat treatment of as-prepared samples. (b) Phase contrast PFM images after heat treatment of as-prepared samples. (c) The analysis of the polarization orientation for the phase images of as-prepared samples shown in (a, b). (d, e) Phase contrast PFM images before and after heat treatment of the ceramic abraded by 5000-grit abrasive paper. (f) The analysis of the polarization orientation for the phase images of abraded samples shown in (d, e).

discussions, that is, abrasion largely removes the polarized surface layers of the as-prepared sample, and subsequent heat treatment restores the polarized surface layer.

4 Conclusions

In summary, the effect of abrasion on the microstructure and properties, especially the flexoelectric response of BT ceramics is investigated. Abrasion produces surface damage and exerts stress on the surface, which induces structural orientation and slightly changes the dielectric properties of the ceramics. More importantly, stress-relaxation was thought to be a mechanism for the generation of polarized surface layers, resulting in the large flexoelectric effect observed in ferroelectric ceramics. Our results suggest that while abrasion-induced stress may have an impact on the measured flexoelectric coefficient of BT ceramics, it is not the main reason for the large flexoelectric coefficient. This study is important for understanding the mechanism of the large flexoelectric response in ferroelectric ceramics.

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Conflict of interest

The authors declare that they have no conflict of interest.

Biographies

Xu Yang is currently a master's student in the Department of Materials Science and Engineering of University of Science and Technology of China under the supervision of Prof. Baojin Chu. Her research mainly focuses on flexoelectric effect of BaTiO₃ ceramics.

Baojin Chu is currently a Professor at the University of Science and Technology of China. He received his Ph.D. degree from Pennsylvania State University in 2008. His current research interests include ferroelectric, piezoelectric, and dielectric materials and applications.

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