

Delayed crack propagation in barium titanate single crystals in humid airBing Jiang,^{1,a)} Yang Bai,¹ Jiang-Li Cao,¹ Yanjing Su,¹ San-Qiang Shi,² Wuyang Chu,¹ and Lijie Qiao¹¹*Corrosion and Protection Center, Key Laboratory of Environmental Fracture (Ministry of Education), University of Science and Technology Beijing, Beijing 100083, People's Republic of China*²*Department of Mechanical Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong*

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Domain witching of ferroelectrics under mechanical or electric load in vacuum or dry air has been intensively studied. However, the effects of environments on the domain switching in ferroelectrics have not been well understood. Here, we demonstrate that domain configurations in BaTiO₃ single crystal under sustained load can be significantly affected by the humidity due to the decrease in surface energy and electrostatic energy upon adsorption of polar water molecules. Consequently, the crack propagation behaviors of the ferroelectrics under sustained load can be remarkably altered.

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Ferroelectrics have triggered much attention for their applications such as microelectromechanical systems, actuators, transformers, and sensors in smart structures. However, one of the main disadvantages for ferroelectrics in such applications is that after long-term working under mechanical field or electric field, cracks may nucleate and propagate. The cracks in ferroelectrics can result in the degradation of the devices. The crack nucleation and propagation in ferroelectric materials are closely related to the domain configurations.¹⁻³ In recent years, much effort has been dedicated to clear understanding of the crack growth and domain switching around crack tips in ferroelectrics under mechanical or electric field.¹⁻⁷ However, most of these studies were carried out in normal environments. In practice, ferroelectric devices are frequently used in some special environments such as humid air. Therefore, it is imperative to study the mechanical degradation mechanisms of ferroelectrics in these environments to improve their reliability.

Previously, the delayed crack propagation in Pb(Zr,Ti)TiO₃ and BaTiO₃ ceramics under external stresses in humid air has been observed.⁸⁻¹¹ By contrast, the delayed crack propagation does not occur in dry air. So far, the effects of the humidity on the crack growth and domain switching in ferroelectrics remain unclear yet. Therefore, in the present study, the delayed crack propagation correlated with the domain switching around the crack tips in BaTiO₃ single crystals in humid air under sustained load was investigated.

A square BaTiO₃ single crystal with a size of 5 × 5 × 1 mm³ was used. First, the upper and lower (001) surfaces were carefully polished. Second, the single crystal was poled along the [010] direction. It means that the polarization is in plane and the domain is referred to as the *a* domain. Third, a penetrated notch of 0.3 mm wide and 1 mm long was pre-fabricated at the center of the 5 mm long edge. Then, an

increasing tensile load was gradually applied to the single crystal along the [100] direction by using a homemade apparatus.¹² The load was stopped when some cracks appeared around the tip of the penetrated notch. A Digital Instruments Nanoscope III atomic force microscope (AFM) and an Olympus polarized light microscope (PLM) were used to examine the crack propagation and domain switching around the crack tips.

Two types of domain configurations were generated around the crack tips, i.e., *a-b* domains and *a-c* domains. The domains in which all dipoles are aligned parallel to the [010], [100], and [001] directions are defined as *a*, *b*, and *c* domains. After the observations using AFM and PLM, the single crystal sample was placed into dry air with a relative humidity (RH) of 2%. No changes to the crack and domain structure were observed within 2 days. Then, the sample was moved into humid air with a RH of 80%. It was observed that the cracks in *a-b* domains propagated with increasing time, while the cracks in *a-c* domains remained unchanged.

Figure 1(a) shows a PLM image of the *a-b* domain configuration around a crack tip. As the vectors of polarization of *a* and *b* domains are perpendicular to each other, the *a-b* domain structure can be observed by PLM because of the light reflection at the domain walls.^{13,14} The dark areas are the original *a* domain matrix, while the bright stripes are *b* domains being generated under the tensile load. However, the *a-b* domain structure cannot be observed by AFM because there is no morphological contrast. The crack propagated with increasing time. With the crack propagation, the domain *A* became longer and a new domain *B* was generated at the crack tip after 6 h, as shown in Fig. 1(b). Actually, the domain *B* slightly moved along with the crack tip and became longer, as shown in Fig. 1(c). As time is further increased, the crack gradually propagated and a new domain *C* appeared at the crack tip, as shown in Fig. 1(d). After 60 h, no changes to the crack and domain configuration occurred around the crack tip.

It is proposed that the adsorption of polar H₂O molecules on the sample surface should be responsible for the

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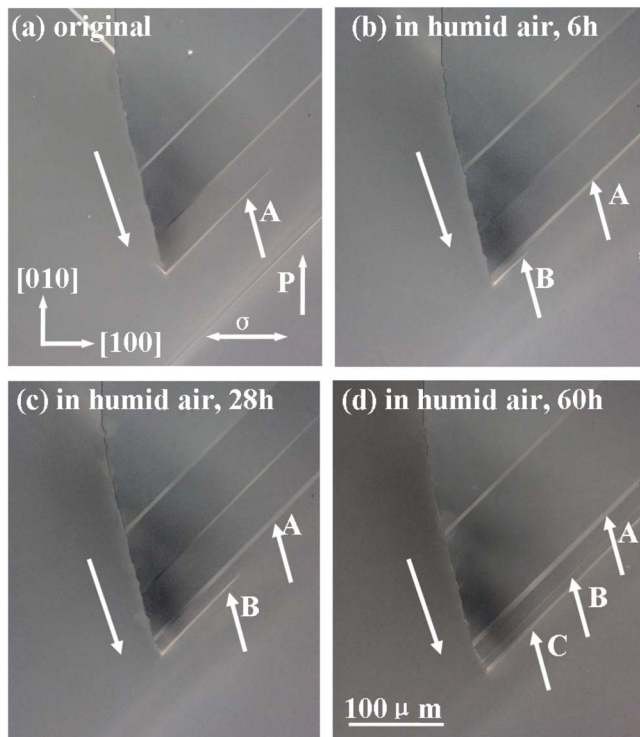


FIG. 1. (Color online) Delayed crack propagation and a - b domain switching around a crack tip in humid air under sustained load observed by PLM at (a) 0, (b) 6, (c) 28, and (d) 60 h.

delayed crack propagation in humid air.⁸⁻¹⁰ The adsorption of H_2O molecules on the two sides of the cracks can reduce the surface energy of the sample, thereby reducing the critical stress needed for the crack growth. The critical stress for the crack growth refers to the stress intensity factor K_I according to the Griffith theory, as given by Eq. (1),

$$\frac{(1 - \nu^2)K_I^2}{Y} = 2\gamma_0 \quad (1)$$

where K_I is the stress intensity factor, γ_0 is the surface energy, ν is the Poisson ratio, and Y is Young's modulus.¹⁵ The stress intensity factor K_I will decrease upon to the surface energy reduction induced by the adsorption of H_2O molecules. Thus, the cracks in a - b domains propagated under sustained load.

However, the cracks in a - c domains did not propagate in humid air under sustained load. Figure 2(a) shows an AFM image of the a - c domain structure around a crack tip. In tetragonal barium titanate, c domains are higher than a domains on the surface. Therefore, the white and higher stripes are c domains, while the dark and lower areas are a domains in AFM images.¹⁶ No b domains were observed around the crack by PLM. Although the crack did not propagate with increasing time, the a - c domain structure around the crack tips significantly changed. After 2 h in humid air, two new c domain stripes of A and B appeared before the crack tip, as indicated by the white arrows in Fig. 2(b). The c domain stripes of A and B became bigger with increasing time in humid air, as shown in Fig. 2(c). With further increasing time, more c domain stripes such as domain stripes of C and D were generated and the original c domain stripes before

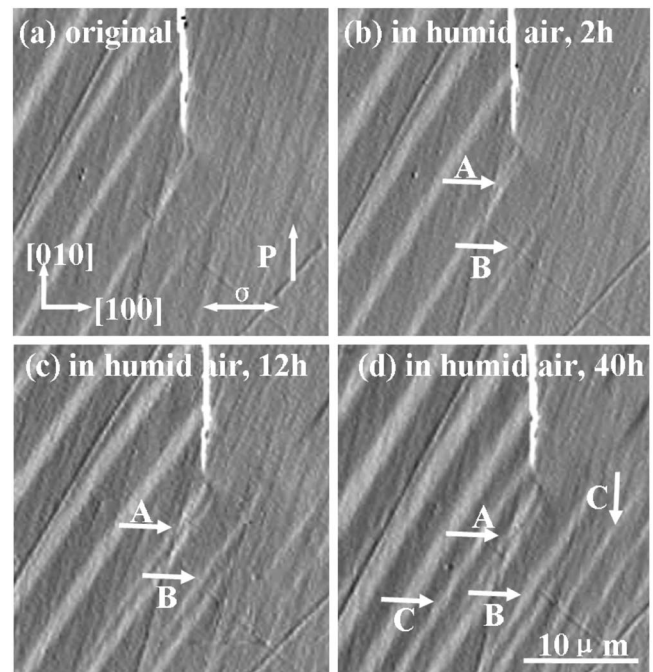


FIG. 2. Evolution of the a - c domain configuration around a crack tip at (a) 0, (b) 2, (c) 12, and (d) 40 h in humid air.

the crack tip became even bigger, as shown in Fig. 2(d). After 40 h, the domain structure did not change any more.

These results indicate that the humidity has different effects on the a - c and a - b domains under sustained load, which result in different crack propagation behaviors. Domain configurations in equilibrium depend on the mechanical and electrical boundary conditions in ferroelectrics. In dry air, under mechanical stress, the generation of new domains and domain switching will occur to relax the stress. In return, electrostatic energy and domain wall formation energy will increase, retarding the domain generation and switching. Thus, there is a competition among the elastic energy (W_M), electrostatic energy (W_E), domain wall formation energy (W_{DW}) and the surface energy (W_S), to minimize the total energy (W_{tot}), as given in Eq. (2),

$$W_{tot} = W_M + W_E + W_{DW} + W_S = \text{minimum}. \quad (2)$$

Because of the increasing load around the penetrated notch at the beginning of the experiment, b and c domains were generated in the original a domain matrix near the crack tips. When the tensile load was held up, the domain configurations around the crack tips remained unchanged and the cracks stopped propagating, which is an equilibrium state for both the domain configurations according to Eq. (2) and the crack length according to Eq. (1). However, once the sample under the sustained load was moved into humid air, the equilibrium was broken because of the reduction in the surface energy upon the adsorption of H_2O molecules.

For the current case, there are two possible ways for the equilibrium state be the retrieved. One way is that the stress could be relaxed by the destructive crack growth until a value smaller than the reduced stress intensity factor K_I , if the domain switching alone cannot relax the stress. This is the case for the crack propagation in a - b domains, as shown

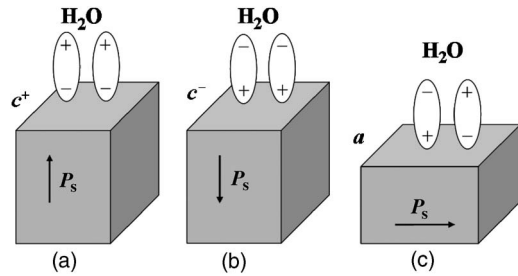


FIG. 3. Schematics for the adsorption of H₂O molecules on *c* and *a* domains.

in Fig. 1. The other way is the relaxation of the stress through changes in the domain configurations including the nucleation and growth of new domains and size changes in the original domains. Consequently, the cracks may not propagate, which is the case, as shown in Fig. 2. Generally, domain formation will lead to an increase in the free energy of the sample.¹⁷ However, considering that the polarization in *c* domains is perpendicular to the sample surface, whereas the polarization in *a* (*b*) domains is in plane, the adsorption of polar H₂O molecules reduced not only the surface energy but also the electrostatic energy of the *c* domains, as illustrated in Figs. 3(a) and 3(b). Thus, the *a-c* domain switching was promoted by the adsorption of polar H₂O molecules, which helped us to relax the stress at the crack tips. Therefore, the cracks in *a-c* domains did not propagate. By contrast, the adsorption of polar H₂O molecules reduced only the surface energy of the *a-b* domains, as shown in Fig. 3(c), thereby leading to the delayed crack propagation. Thus, the

different adsorptions of polar H₂O molecules on *a*(*b*) and *c* domains give an answer to the different crack propagation modes in BaTiO₃ single crystals under sustained load in humid air.

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