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Etching-enhanced growth of indentation crack in barium titanate single crystal

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Abstract

The effect of etching on an unloaded indentation crack in a poled $BaTiO_3$ single crystal whose poling direction is lying in or normal to the indentation plane, has been investigated. The result showed that for the sample whose poling direction was lying in the indentation plane, the indentation cracks and 90° domain switching zones surrounded by two pairs of indentation cracks grew gradually during etching using HCl+HF aqueous solution, and reached saturation after etching for 30 s, however, the effect of etching on the crack length and the size of the domain switching zone was very small for the sample whose poling direction was normal to the indentation plane. Etching-enhanced domain switching and crack propagating is due to adsorption-decreased surface energy.

Keywords: Etching-enhanced domain switching; Indentation crack; $BaTiO_3$

1. Introduction

For poled ferroelectric ceramics, fracture toughness anisotropy was revealed by Vickers indents. Cracks propagating parallel to the poling direction were considerably shorter than that perpendicular to the poling direction [1–7]. The effect has been variously explained by either domain switching at the crack tip [1–5] or residual stress brought about during poling [6,7]. Ferroelectric single crystals are usually transparent and contain large size domains, and then domain switching and crack propagating can be easily observed *in situ* by using polarized light microscopy [8,9].

By indenting on a poled $BaTiO_3$ single crystal whose poling field was lying in the observation plane, Busche and Hsia [8] reported that cleavage fracture took place on the {113} planes nearly perpendicular to the poling direction, and extensive domain switch observed around the arrested crack tips was caused by the compressive radial stress field surrounding the indentation. Fang and Yang reported different domain switching patterns and indenting crack orientation for $BaTiO_3$ single crystals poled in different directions [9]. For anti-plane poling sample whose poling field is normal to the observation plane, indentation cracks emanated equally from the indenting pyramid in four directions, and domain bands perpendicular to the indenting cracks were formed [9]. For the sample whose poling field is lying in the observation plane, however, two pairs of long cracks nearly perpendicular to the poling direction emerged from the two opposing indentation corners normal to the poling direction; and the domain switching occurred in the zones surrounded by the two pairs of cracks [9]. *In situ* TEM study of electric field-induced micro-cracking in PMN-PT, i.e., $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$, single crystals showed that the field-induced cracking preferred to propagate along the ferroelectric domain wall [10].

Li et al. studied the domain switching in a single edge notched beam of PMN-PT single crystal under electromechanical loading [11]. The result showed that 90° domain switching zone was always situated near the crack tip due to the electromechanical field concentration, and the more acute the crack tip was, a larger 90° switching zone appeared near the crack tip. The switching zone did not disappear after the electric and mechanical loading was removed [11].

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In situ observation of electrically induced fatigue crack growth together with domain switching was carried out for $BaTiO_3$ single crystal under alternating electric field [12]. The result showed that the crack propagation behavior was a repeated process of continuous but small increments followed by a sudden increase in the crack length, and parallel lines of 90° domain boundaries appeared and disappeared alternatively around the crack during cycling [12].

If a polished surface of $BaTiO_3$ single crystal is etched using HCl+HF aqueous solution, domain switching zones could be clearly revealed. Experiment found accidentally that an indentation crack can propagate and the domain switching zones enlarge during etching. The objective of this paper is to investigate the rule and mechanism of etching-enhanced domain switching and indention crack propagating in $BaTiO_3$ single crystal.

2. Experimental procedure

Poled $BaTiO_3$ single crystals with the size of 5×5×1 mm were provided by the Institute of Physics, Chinese Academy of Science. The poling direction was lying in or perpendicular to the indentation plane. Indentations were performed with a 1.96 N load and a dwell time of 20 s. The etching solution was 14%HCl+14%HF+72%H_2O (in volume percent).

3. Experimental results

For the sample whose poling direction is lying in the indentation plane, indentation cracks and the domain switching zones surrounded by two pairs of cracks grow gradually during etching, and reach saturation after etching for 23 s, as shown in Fig. 1. Fig. 1 shows that crack tips propagate from A, B, F, G to A_1, B_1, F_1, G_1 and A_2, B_2, F_2, G_2, respectively after etching for 3 and 13 s. Fig. 2 is differential interference contrast (DIC) image and polarized light image of the other indentation crack after etching for different time. Fig. 2 shows also that indentation cracks and the "c" domain switching zones surrounded by two pair of cracks grow continuously during etching, and reach saturation after etching for 30 s.

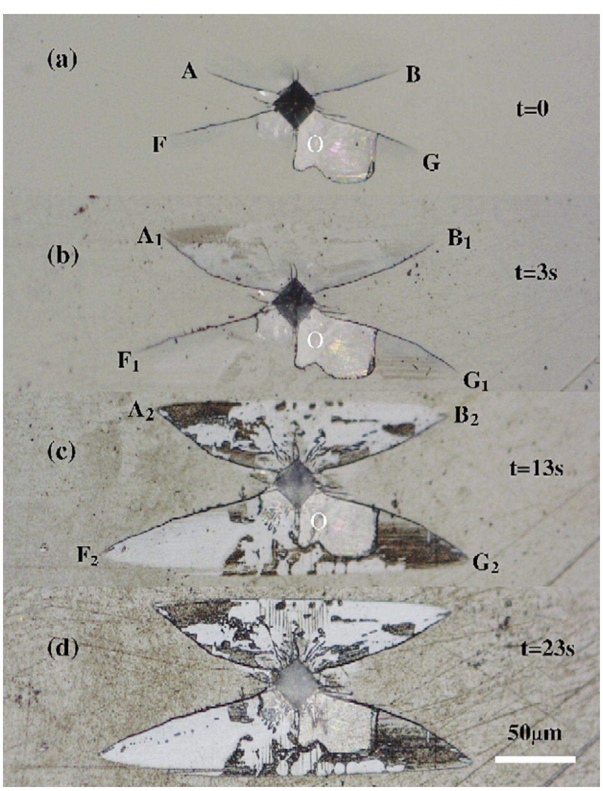

Fig. 1. Optical micrographs of indentation crack after etching for different time; the poling direction is vertical.

For the sample whose poling direction is lying in the indentation plane, the average size of 16 indentation cracks increased from 140 μm to 216 μm after etching for 30 s, and the 95% confidence interval of the average size were ±9 μm and ±7 μm, respectively.

For anti-plane poled sample whose poling direction is normal to the indentation plane, the effect of etching on the crack length and the domain switching zone is very small, as shown in Fig. 3. The means and 95% confidence interval of 16 indentation cracks before and after etching for 30 s were 65±5 μm and 68±5 μm, respectively.

4. Discussion

The fracture toughness during indentation can be obtained using the following equation [13,14],

$$K_{\mathrm{IC}} = \beta\left(\frac{E}{H}\right)^{1/2}\left(\frac{P}{C^{3/2}}\right) \tag{1}$$

where H is the hardness, E the Young's modulus, P the indentation load, $2c$ the length of the indentation crack and β=0.04 [13] or 0.016 [14].

The stress intensity factor induced by the residual stress in an unloaded indentation crack, K_r, is equal to the fracture toughness K_{IC} [14], thus

$$K_{\mathrm{r}} = K_{\mathrm{IC}} = \beta\left(\frac{E}{H}\right)^{1/2}\frac{P}{c^{3/2}} \tag{2}$$

For the $BaTiO_3$ single crystal, the Griffith theory is suitable as no dislocation movement take place at room temperature, thus for an unloaded indentation crack [15],

$$G_{\mathrm{I}} = \frac{(1-\nu^2)K_{\mathrm{r}}^2}{E} = \frac{\beta^2(1-\nu^2)P^2}{Hc^3} = 2\gamma \tag{3}$$

where γ is the surface energy.

During etching using the HF+HCl aqueous solution, the surface energy γ will be decreased continuously with increasing time until reaching a saturation value γ_{th}. With decreasing the resistance for crack propagation, i.e., 2γ, the drive force for crack extension, i.e., $(1-\nu^2)K_r^2/E$, will be larger than the resistance, which resulted in propagation of the indentation crack during etching. With propagating of the crack, i.e. increasing c, the stress intensity factor of the propagating crack decreases because of $K_r \propto c^{-3/2}$, which resulting in arresting. Based on Eq. (3), when the surface energy decreases from γ to γ_{th}, the length of crack will increase from c_0 to c_{th}, i.e.,

$$\frac{\beta^2(1-\nu^2)P^2}{H} = 2\gamma c_0^3 = 2\gamma_{\mathrm{th}}c_{\mathrm{th}}^3 \tag{4}$$