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Anisotropic microhardness in single-crystal and polycrystalline $BaTiO_3$

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The room-temperature hardness of single-crystal and dense polycrystalline $BaTiO_3$ was investigated by microindentation. The longer diagonal of the Knoop indenter was oriented either parallel or perpendicular to the poled axis of the material. The hardness of the unpoled sample was isotropic. However, hardnesses in the poled samples were anisotropic, with the highest hardnesses resulting when the longer diagonal was parallel to the poled axis. The hardness anisotropy may be due primarily to residual stresses caused by the piezoelectric coupling effect. © *1998 Chapman & Hall*

1. Introduction

The perovskite-type oxide $BaTiO_3$ is a ferroelectric whose electrical properties have been studied extensively because of its many technical applications, including sensors, transducers and actuators [1–5]. The technological importance of $BaTiO_3$ has been demonstrated repeatedly, and its physical properties in ceramic form have been thoroughly investigated.

Generally, the various properties of ferroelectric materials depend on the domain configuration. During electrical poling, for instance, a strong field tends to align the domains, which remain aligned after removal of the electric field, resulting in a remnant polarization [6]. Because the 90° domains in tetragonal ferroelectric ceramics are generated to minimize the internal stress developed at the Curie temperature [6, 7], application of external stress can change the 90° domain orientation and, therefore, the properties of the ceramics [8].

It has been shown that the electrical properties of the ferroelectric materials change with external stress and thus have been explained by a possible change in domain orientation [9–12]. Recently, Li *et al.* [13] reported a high degree of anisotropy in the elastic and electromechanical properties of single-crystal $BaTiO_3$. Extending this work, Li *et al.* [8] reported the manipulation of 90° domain walls by application of applied stress. Using micro-Raman spectroscopy, they observed the rotation of the crystallographic axis associated with 90° ferroelectric domains by the application of uniaxial compressive stress perpendicular to either the (0 0 1) or the (1 0 0) face of single-crystal $BaTiO_3$ and $PbTiO_3$.

In most applications, ferroelectrics are subjected to stress conditions by mechanical and applied electric fields, and they can fail catastrophically because of low fracture toughness [14–17]. Many studies have shown that poled piezoelectric ceramics exhibit an anisotropic fracture toughness [16–19]. It might be expected that this anisotropy would be reflected in other mechanical-property measurements, e.g., hardness. However, no studies have been conducted to investigate the relationship between room-temperature hardness and domain configuration in poled $BaTiO_3$. Therefore, this study was undertaken to explore the relationship between domain orientation and hardness. The study measures hardness as a function of orientation of the Knoop indenter with respect to poling direction in single-crystal and polycrystalline $BaTiO_3$.

2. Experimental procedure

High-density polycrystalline $BaTiO_3$ specimens were prepared from reagent-grade $BaTiO_3$ powder having an average particle size of 1.1 μm (Johnson & Matthey; purity, 99.9%). The powders were isostatically pressed into rectangular bars by using a pressure of about 200 MPa for 5 min. The resulting compacts were then sintered at 1360 °C for 1 h in flowing O_2 and for 1 h in air with a heating rate of 200 °C h^{-1} and a cooling rate of 60 °C h^{-1}. The densities of the samples were 98–99% of the theoretical density. For the Knoop indentation test, polycrystalline $BaTiO_3$ samples measuring approximately 3 mm × 3 mm × 25 mm were cut from the sintered specimens. Surfaces were polished on a standard metallographic wheel using diamond pastes to achieve a mirror-like surface finish that contained only a few well-dispersed very fine pores. Samples were annealed at 250 °C for 4 h to relieve residual stresses generated during the cutting, grinding and polishing processes. For poling, gold electrodes were sputtered onto a pair of opposite major faces of the samples for 10 min. In poling, an electric field was applied to the electrodes while the sample was immersed in silicone oil; 1 kV mm^{-1} was applied for 1 h to switch domains. Poling was performed at room temperature and 80 °C. For further removal of the 90° domain, a compressive stress was applied to the *a* or *b* direction of the sample.

The $BaTiO_3$ single crystals used in the study were purchased from the Institute of Physics, Chinese Academy of Science, Beijing. These crystals were grown by the top-seed solution method and were poled in a direct-current electric field to obtain a single domain. As received, they were optically clear and free of gross imperfections and twins when examined under a cross-polarized light microscope. Conditions for poling of single crystals were the same as those for the polycrystals.

For the dielectric measurement, samples were held in a Hewlett–Packard 16034 test fixture, which was connected to a computer-controlled Hewlett–Packard (San Jose, CA) 4192A impedance analyser. The dielectric constant, ε, and dielectric loss, tan δ, were determined automatically, with the frequency sweeping logarithmically from 10 Hz to 13 MHz.

For the Knoop indentation tests, loads from 0.25 to 10 N were applied to the sample for 15 s by a commercial microhardness testing machine (Micromet 2003, Buehler, Lake Bluff, IL). The Knoop indentations were applied to the samples randomly without selecting particular grains. The indentation impression sizes were measured immediately after unloading. To study the relationship between domain orientation and hardness, the longer diagonal of the Knoop indenter was aligned either parallel or perpendicular to the poled axis of the material.

3. Results and discussion

Fig. 1 shows the microstructure of polycrystalline $BaTiO_3$ sintered at 1360 °C for 2 h. The grain size is approximately 60 μm, and 90° domains are visible in the structure. An optical micrograph of the single crystal is shown in Fig. 2. The 90° domains shown in the image were removed before testing.

The electrical properties of the samples were measured in order to characterize the $BaTiO_3$ further. The coercive field, E_c, of a sample sintered at 1360 °C was approximately 0.15 kV mm^{-1}, equal to reported values [20]. The dielectric constant, ε, and dielectric loss, tan δ, and polarization–electric field (*P–E* hysteresis) behaviour were measured before and after room-temperature poling. Fig. 3 shows the dielectric constant and loss for a polycrystalline specimen sintered at 1360 °C before and after mechanical detwinning, as a function of frequency. Fig. 3b shows the anisotropic dielectric constant with the direction of the sample after mechanical detwinning; ε_{33} and ε_{11} are the dielectric constants parallel and perpendicular, respectively, to the poling direction. It should be noted that the dielectric loss of the sample is

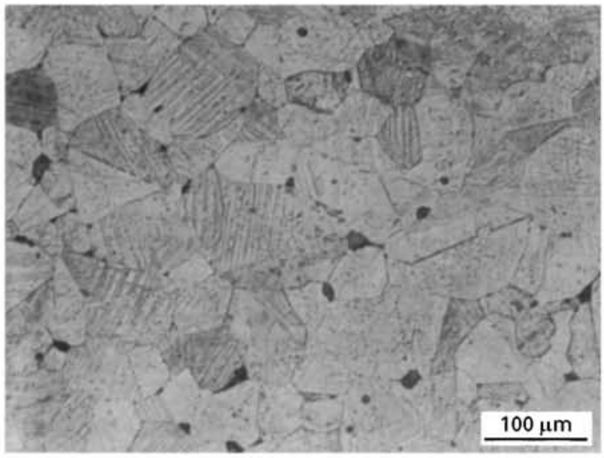

Figure 1 Microstructure of polycrystalline $BaTiO_3$ sintered at 1360 °C for 2 h.

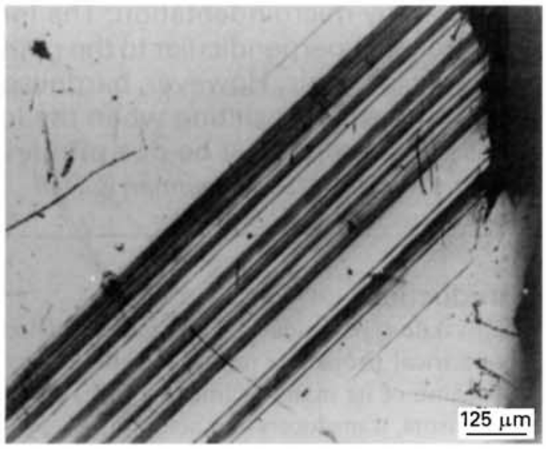

Figure 2 Microstructure of single-crystal $BaTiO_3$.

extremely small, indicating the high quality of the polycrystalline sample.

Table I shows ε_{33} and ε_{11} as functions of poling conditions at 100 kHz frequency. The perpendicular dielectric constant, ε_{11}, is much higher than the dielectric constant, ε_{33}, parallel to the poled axis for single-crystal $BaTiO_3$. The dielectric constants for the polycrystalline $BaTiO_3$ are isotropic after poling at both room temperature and 80 °C. However, applying a stress reduces ε_{33} while ε_{11} remains unchanged. This indicates that 90° domain switching occurred as a result of the applied stress.

Fig. 4 shows the positioning of the Knoop indenter. The long diagonal of the indent was positioned on the poled specimens so that it was either perpendicular (Fig. 4a) or parallel (Fig. 4b) to the poled axis of the material. More than 20 indentations were made at each load from 0.25 to 10 N. The Knoop microhardness, H_K, was determined from the diagonal, *d*, and the load, *P*, using

$$H_K = \frac{14\,229P}{d^2}\ \text{(GPa)}$$

where the force *P* is in newtons and *d* is in micrometres. In the following section, $H_\perp$ represents the

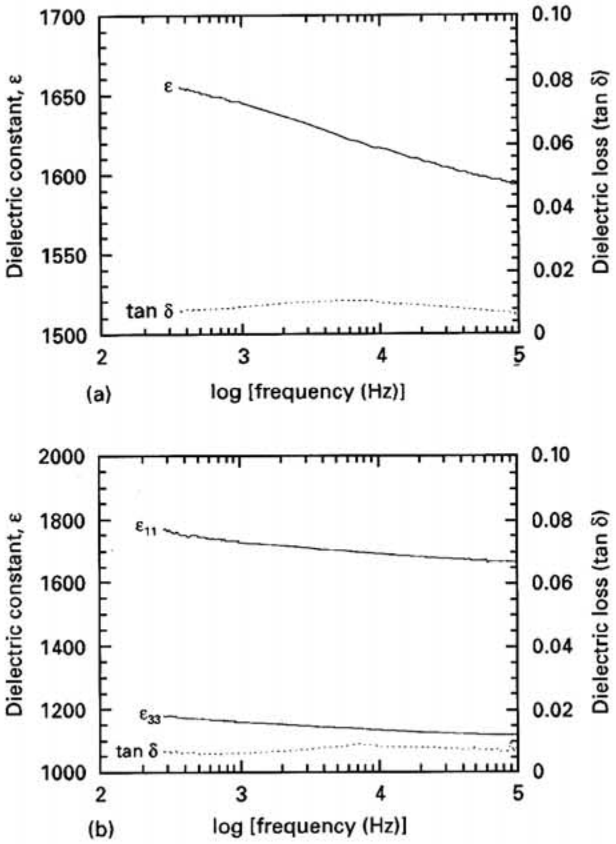

Figure 3 Dielectric constant, ε, and dielectric loss, tan δ, for polycrystalline $BaTiO_3$ sintered at 1360 °C for 2 h as a function of frequency: (a) before poling; (b) after mechanical detwinning.

TABLE I Dielectric constants as function of conditions of samples sintered at 1360 °C at 100 kHz

Material	Conditions	ε_{33}	ε_{11}
Polycrystal	Sintered	1595	1595
	80 °C poling	1549	1663
	Applied stress	1118	1670
Single crystal	As received	257	1967
	Room-temperature	163	4044
	80 °C poling	216	3421

hardness perpendicular to the poled axis and $H_{\parallel}$ represents hardness parallel to the poled axis.

Fig. 5 shows microstructures of Knoop indentation at loads of 0.25 and 2 N on unpoled polycrystalline $BaTiO_3$. For a load of 0.25 N (Fig. 5a), there is no appearance of a crack at the end of indentation. However, measurements could not be extended above 1 N because of fracture around the indentation. Fig. 5b shows an indentation at a load of 2 N. A fracture is visible on the left-hand side above and below the indentation.

Table II compares average hardness data at loads of 0.25, 0.50 and 1 N of single-crystal and polycrystalline $BaTiO_3$. The microhardness was independent of load. The microhardness of the unpoled polycrystalline $BaTiO_3$ was approximately constant isotropic. However, poling of the polycrystalline samples produced an anisotropic hardness value. The hardness parallel to the poled axis is higher than for an unpoled sample,

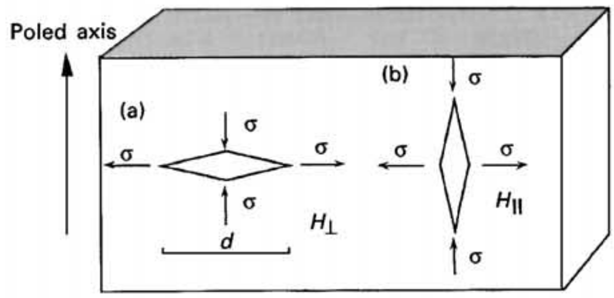

Figure 4 Position of Knoop indenter as a function of poled direction: (a) perpendicular to the poled axis; (b) parallel to the poled axis.

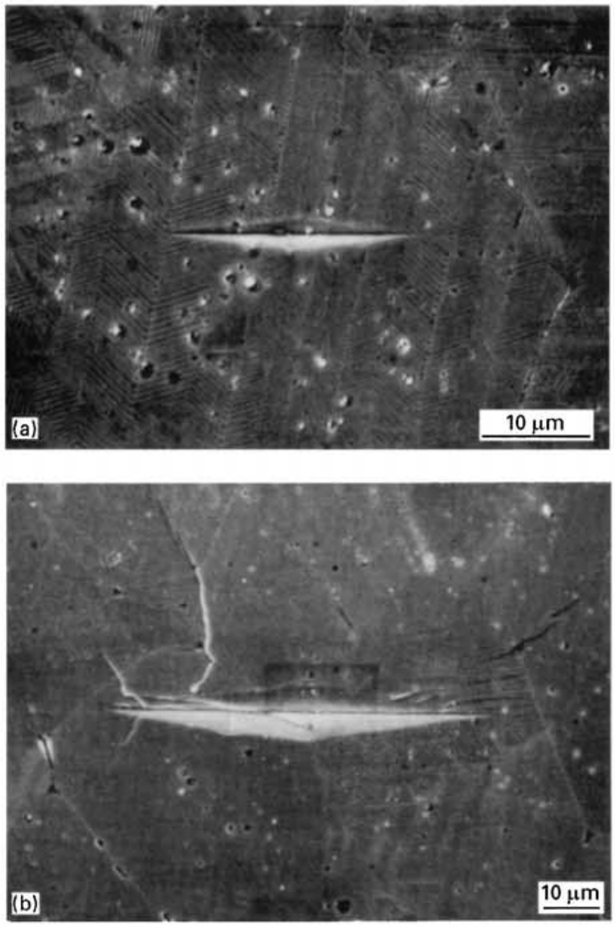

Figure 5 Microstructures of knoop indentations as a function of load on polycrystalline $BaTiO_3$: (a) 0.25 N; (b) 2 N.

and the hardness perpendicular to the poled axis is lower than for an unpoled sample. Single-crystal behaviour was similar to that of the polycrystal, with almost constant hardness at low loads, and $H_{\parallel}$ higher than $H_{\perp}$. The standard deviations of H_K for the polycrystals are 6%, resulting in an overlap of $H_{\perp}$ and $H_{\parallel}$. However, comparison with the single-crystal results, which have much less scatter, is convincing evidence that the trend is correct and that H_K is anisotropic with $H_{\parallel} > H_{\perp}$.

Wang and Singh [21] studied crack propagation behaviour in piezoelectric lead zirconate titanate. They reported that as-fired and unpoled piezoelectric ceramics are isotropic in properties and are under a residual compressive stress. However, poling

TABLE II Knoop microhardness of single-crystal and polycrystalline $BaTiO_3$

Material	Condition	Microhardness (GPa)
Polycrystal	$H_{unpoled}$	4.53 ± 0.27
	$H_{\perp}$	4.42 ± 0.26
	$H_{\parallel}$	4.69 ± 0.28
Single crystal	$H_{\perp}$	4.06 ± 0.09
	$H_{\parallel}$	4.35 ± 0.08

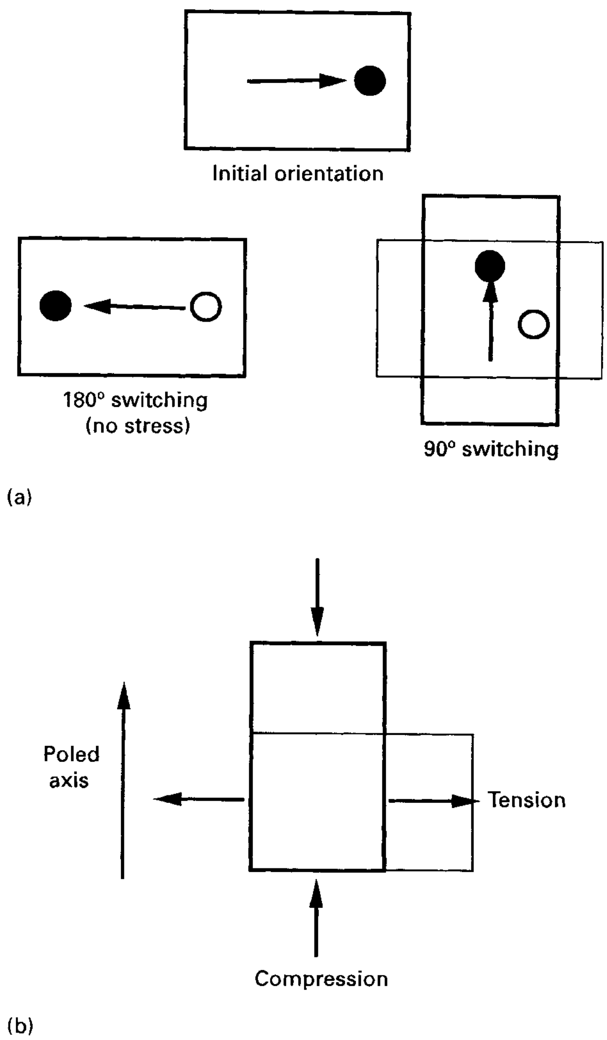

Figure 6 Schematic diagrams showing (a) the change in a unit cell for 180° and 90° domain switching and (b) the mechanism by which stresses are generated by 90° domains [21].

changes the residual stress state, which introduces an anisotropy in crack propagation. Fig. 6 shows schematically the mechanism by which stresses are generated in a unit cell by 90° domain switching. In the case of 180° domain switching, there is no dimensional change during poling; so 180° domain switching is not expected to affect the residual stress state. However, 90° domain switching is accompanied by a local dimensional change within the domain orientations. This dimensional change results in a tensile stress in the direction perpendicular to the poled axis and a compressive stress in the direction parallel to the poled axis. As shown in Table I, the large difference between ε_{11} and ε_{33} after applying a compressive stress indicates piezoelectrically induced switching of 90° ferroelectric domains in tetragonal $BaTiO_3$. An applied tensile stress tends to increase the indentation length, while compression reduces the length. An increased indentation length corresponds to a lower hardness. Therefore, the anisotropic hardness measured in this study is consistent with the residual stress models. The effects of residual stresses on hardness of metals are controversial. Vitovec [22] reported residual stress effects on hardness in type 304 stainless steel and an aluminium bronze while, more recently, Pharr *et al.* [23] claim that residual stress has no effect on hardness in an aluminium alloy (8009). However, work on metals may not be directly applicable to ceramics. The source of residual stresses in the single-crystal $BaTiO_3$ is not clear. The fact that the domains always occur at the same place during repeated cycles gives rise to the speculation that microstructural inhomogeneities could be the source of the residual stresses in the single crystals.

4. Conclusions

The room-temperature microhardness of single-crystal and polycrystalline $BaTiO_3$ was investigated by microindentation. The longer diagonal of the Knoop indenter was oriented either parallel or perpendicular to the poled axis of the material. Poling both the polycrystalline and the single-crystal $BaTiO_3$ produced an anisotropy in the hardness in agreement with a residual stress model.

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