Journal of the European Ceramic Society **12** (1993) 147–151

Effect of External Compressive Stress on the Domain Configuration of Barium Titanate Ceramics

Sang-Beom Kim, Tai-Joo Chung & Doh-Yeon Kim

Department of Inorganic Materials Engineering, College of Engineering (400), Seoul National University,
Seoul 151-742, Korea

(Received 1 September 1992; accepted 1 November 1992)

Abstract

When the sintered $BaTiO_3$ specimens were treated at 200°C and cooled under compressive stress, notable change in domain configuration occurred. As a result of external compressive stress applied during transformation from cubic to tetragonal, the banded domain structure has changed to a simple lamellar one and the 90° domains have aligned. The observed change in domain configuration under external stress has been explained in terms of elastic strain energy minimization.

Gesinterte $BaTiO_3$-Proben, die bei 200°C wärmebehandelt und dann unter Druckspannung abgekühlt wurden, zeigten eine deutliche Veränderung der Domänenkonfiguration. Eine von außen während der Umwandlung von kubisch zu tetragonal aufgebrachte Druckspannung bewirkte eine Umwandlung der räumlich ausgerichteten Domänenstruktur in eine einfache lamellare, die 90° Domänen richten sich aus. Die beobachtete Veränderung der Domänenkonfiguration unter äußerer Druckspannung wurde in Hinsicht Minimierung der elastichen Verzerrungsenergie erklärt.

Quand des échantillons de $BaTiO_3$ denses, soumis à une contrainte de compression, sont chauffés à 200°C et refroidis, des modifications importantes dans la configuration des domaines se produisent. Comme résultat de l'application d'une contrainte de compression externe durant la transformation cubique → quadratique, la structure des domaines en bandes est modifiée en simple lamellaire et les domaines à 90° sont alignés. Les modifications observées dans la configuration des domaines soumis à des contraintes externes sont expliquées en termes de minimisation de l'énergie de déformation élastique.

1 Introduction

One of the intrinsic and unique microstructural features in ferroelectric ceramics, such as barium titanate or lead zirconate titanate, is that their grains consist of domains in which the polar axis (tetragonal axis) of all tetragonal unit cells are in the same direction. Furthermore, it is well known that the various properties of these materials depend critically on the configuration of these domains. During electrical poling, for instance, a strong field tends to align the domains, and the remaining alignment after removal of the field results in a remnant polarization.[1] On the other hand, the fracture behavior of PZT ceramics is also known to depend on the domain configuration.[2]

Since the domains in tetragonal ferroelectric ceramics are generated to minimize the internal stress developed during transformation from cubic to tetragonal at the Curie temperature,[1,3] the application of external stress is predicted to alter the domain configuration and therefore the properties of these ceramics. Note that the tetragonal axis develops along any one of the three original cube axes and thus the application of a uniaxial compressive stress during transformation may favor domains with the tetragonal axis normal to the applied stress. It has been shown, indeed, that the electrical properties of the ferroelectric materials, such as permittivity, vary with the external stress, and the results were explained by a possible change in domain configuration.[4–7] The purpose of this investigation is to establish the direct microstructural evidence of this predicted change in domain structure under external stress. The experiments were carried out with barium titanate ceramics and the specimens prepared by sintering were again treated at 200°C and cooled under compressive stress.

Journal of the European Ceramic Society 0955-2219/93/$6.00

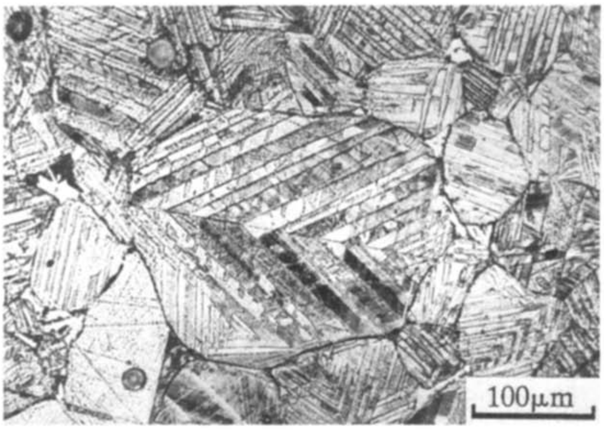
2 Experimental Procedure

The powder used in experiments was commercial grade barium titanate (TAM Ceramics Inc., Niagara Falls, NY, USA) and its physical and chemical characteristics (as determined by the manufacturer) are given in Table 1. The powder was compacted into cylindrical specimens 12·7 mm in diameter under a pressure of 5 MPa and then pressed hydrostatically at 90 MPa. The compacts were sintered at 1400°C for 16 h. During sintering, oxygen gas was used during the heating stage and then changed to air as soon as the sintering temperature was reached. Such an atmosphere change during sintering has been demonstrated to lower the residual porosity of the specimen by enhancing the diffusion of trapped oxygen in the pores.[8] The heating rate for sintering was 4°C/min and the specimens were furnace-cooled after sintering. These conditions resulted in dense specimens with coarse grains from which the domain configuration could be easily observed.

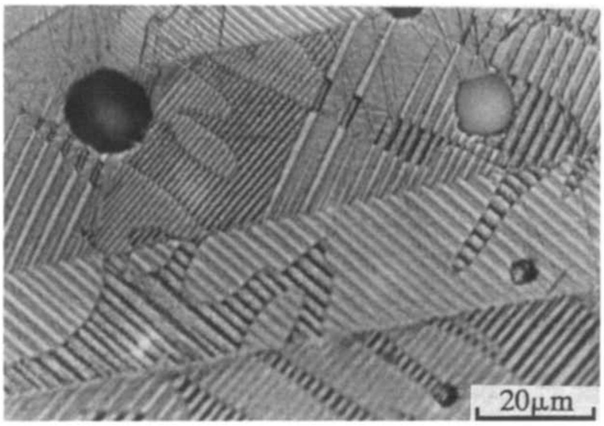
Sintered specimens were then cut into cubes (5 × 5 × 5 mm) by using a diamond saw and polished with 0·05 μm alumina powder for microscopic examinations. Photographs of the polished sections were obtained after etching for 20 min with a solution of 10% HCl containing a little HF.[9] In order to examine the effect of compressive stress on domain configuration, the same specimen was polished again with 0·05 μm alumina powders and then heat-treated at 200°C for 30 min in silicon oil. During cooling to room temperature at a rate of 3°C/min, the uniaxial compressive stress of 20 MPa was applied to the specimen using a hydraulic press. The stress was removed at about 40°C and then the specimen was etched for microstructure observation. This heat-treatment at 200°C has been expected to lead to a complete transformation from tetragonal to cubic. The Curie temperature of $BaTiO_3$ is about 125°C and domains are known to be mobile even some 10 K below it.[10]

Table 1. Physical and chemical characteristics of the $BaTiO_3$ powder used

Component	*wt%*
BaO	65·60
TiO_2	34.23
Al_2O_3	0·02
SiO_2	0·01
Fe_2O_3	0·006
SrO	0·07
Na_2O	0·01
SO_3	0·025
CO_2	0·17
Average particle size (μm)	1·5
Ba/Ti ratio	0·9986



(a)



(b)

Fig. 1. Microstructures of the $BaTiO_3$ specimen sintered at 1400°C for 16 h under (a) low and (b) high magnification.

3 Results and Discussion

Figure 1(a) and (b) are the microstructures of the barium titanate specimen obtained after sintering (under low and high magnifications, respectively). The determined average grain diameter was 110 μm and its porosity was about 2%. The domains are easily discerned in these micrographs and their complicated configuration has already been the subject of a number of studies.[3,11–16] The grains are, in fact, under constrained condition during phase transition and thus the 90° domains in a herringbone pattern (the fine parallel lines of a few tens μm in length) are mainly generated to minimize the elastic energy. It can be also noted in Fig. 1(b) that there are many 180° domains of irregular shape, which are usually referred to as a watermark pattern. In a coarse-grained barium titanate, such as obtained in this experiment, the observed banded domain structure is known to be energetically more favorable than the simple lamellar one.[3]

Figure 2 is the microstructure of the same area as Fig. 1(a), but the specimen has been treated again at 200°C and cooled to room temperature under the uniaxial pressure of 20 MPa. Since this microstructure was obtained from the section already

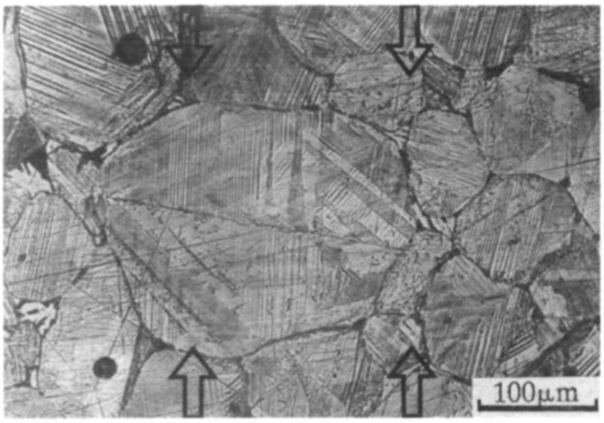


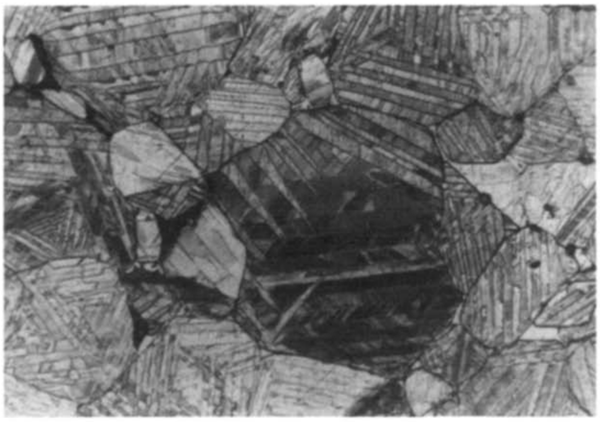
Fig. 2. The same section as Fig. 1(a) obtained after the retreatment at 200°C and cooled under the compressive stress. The stress direction is indicated by the arrows.

examined, approximately 10 μm in depth was again removed from the surface shown in Fig. 1(a). The same section which had been observed previously could be found without difficulties from the shape of grains and the pore location. In order to exclude a possible aging effect[17,18] on domain structure, the microstructure was examined within 2 h after the release of pressure. In fact, the domain structure observed in Fig. 2 was not greatly changed by aging at room temperature for few days.

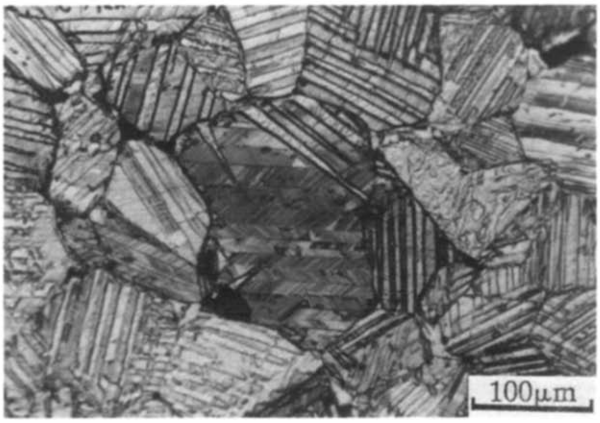
Comparing the domain configuration of the grains before and after the treatment, it can be easily noted that the external pressure applied during phase transformation leads to a significant change in domain configuration. A banded structure (Fig. 1(a)) has changed to a simple lamellar one (Fig. 2) and the density of domains has greatly decreased with the practical disappearance of 180° watermark patterns. In particular, the 90° domain walls in the central large grain in Fig. 1(a) were observed to align in parallel with the applied stress (Fig. 2). On the other hand, the straight line which extends completely from left to right through that grain is expected to be the boundary of (111) growth twins.[13]

Note, however, that the microstructure shown in Fig. 1(a) represents the grains inside the specimen, which were clamped three dimensionally during phase transformation, while that of Fig. 2 is for the grains clamped in two dimensions. As a consequence, the difference in distribution of internal stress imposed on the grains during phase transformation may also lead to the change in domain structure. In order to check for such a possibility, the domains formed in the surface grains have been compared with those of the interior grains. Figure 3(a) shows the microstructure of the specimen after sintering and Fig. 3(b) is the same set of grains after treatment at 200°C. For this case, however, the specimen was cooled to room temperature without applying any pressure.

Both the grains at the interior and at the surface of the specimen show the banded structure. The domain density in Fig. 3(b) is somewhat lower than that in Fig. 3(a), which can be associated with the slight difference in internal stress condition during the phase transformation. The grains surrounded three dimensionally are expected to have more restraint than those at the surface. In addition, the change observed from Fig. 1(a) and Fig. 2 is not expected to be the consequence of polishing because fine alumina powders (0·05 μm) were used in this experiment. It has indeed been shown that the polishing with fine abrasives does not cause the domain reorientation.[13,19]



(a)



(b)

Fig. 3. Microstructures of the specimen: (a) the domain configuration formed under three-dimensionally clamped conditions and (b) the same section as (a) but the domains are formed under free surface conditions.

Therefore, the change in domain configuration observed from Figs 1(a) to 2 is mainly caused by the external pressure applied during phase transformation. Figure 4 illustrates the unit spatial domain configurations (without considering the irregular 180° watermark patterns) of barium titanate,[3,12] for which the 90° domain walls are {101} planes and thus the cube is composed of {001} planes. Without any external pressure during the phase transformation, a grain would consist of both domain configurations illustrated in Fig. 4(a) and (b). When an external pressure is applied during transform-

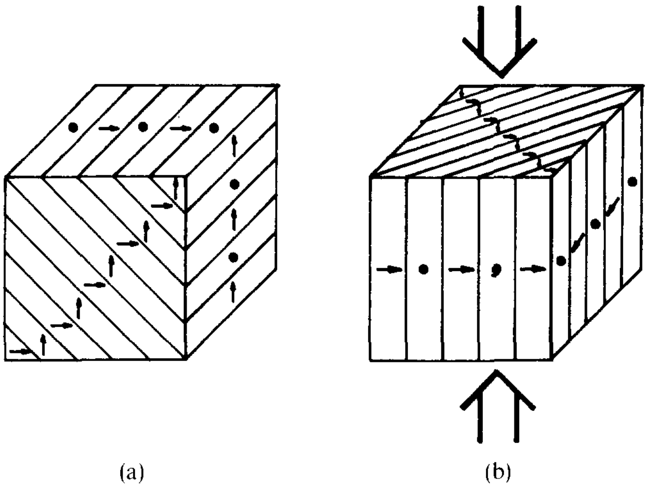


Fig. 4. Schematics of domain configuration of barium titanate ceramics: both (a) and (b) are possible under normal conditions but (b) would be dominant under the external compressive stress.

ation, on the other hand, all the tetragonal axes tend to be perpendicular to the applied pressure for minimizing the elastic strain energy. As a result, the domain configuration illustrated in Fig. 4(b) is expected to be dominant. Even under such stressed conditions, however, the domain patterns may vary from grain to grain since the individual grains are randomly oriented in the specimen. The 90° domain walls are consequently expected to align most and in parallel with the direction of pressure when $\{001\}$ planes of the grain are parallel to the external pressure. In this regard, the surface of the central large grain in Fig. 2 is believed to be such a case.

By considering the elastic and the domain wall energy as a function of grain size, it has been shown[3,14] that the domain structure varies with the grain size: the simple lamellar structure for fine-grained barium titanate and the banded one for the coarse-grained barium titanate. The results obtained in this experiment, however, may indicate that the inhomogeneity of internal stresses by mutual interaction between adjacent grains is the major cause of the banded domain structure. When such internal stresses are smaller than the external stress, the simple lamellar domain structure is expected to prevail regardless of the grain size. On the other hand, the disappearance of 180° watermark patterns at the plane parallel to external stress is not easily understood because the mechanical stress itself has been known[7] to cause only the change in 90° domains. The observed change in domain configuration by external stress would naturally result in the change in various dielectric properties of barium titanate, as has been reported already.[4–7] A similar effect of external pressure on ferroelastic twinned structures is expected and, in fact, the detwinnings in Y–Ba–Cu–O[15] and tetragonal ZrO_2 single crystals[16] as a result of external pressure have been observed.

4 Conclusion

This study has demonstrated microstructurally that the domain configuration of barium titanate ceramics is greatly changed by a uniaxial compressive stress applied during the phase transformation from cubic to tetragonal. Since the domains with tetragonal axis normal to the direction of compressive stress have the lowest elastic energy, the 90° domains were observed to align by the external compressive stress. Furthermore, a simple lamellar domain structure has been obtained instead of the banded domain structure and its density, particularly that of 180° watermarks, has greatly decreased. The inhomogeneity of internal stress by mutual interaction with surrounding grains is expected to be the main cause of the banded domain structure with high domain density in barium titanate cooled without load.

Acknowledgement

This work was supported by the Korea Science and Engineering Foundation through the Center for Interface Science & Engineering Materials.

References

1. Jaffe, B., Cook Jr, W. & Jaffe, H., *Piezoelectric Ceramics*. Academic Press, NY, 1971, pp. 53–114.
2. Kim, S.-B., Kim, D.-Y., Kim, J.-J. & Cho, S.-H., Effect of grain size and poling on the fracture mode of lead zirconate titanate ceramics. *J. Am. Ceram. Soc.*, **73**(1) (1990) 161–3.
3. Arlt, G., Twinning in ferroelectric and ferroelastic ceramics: stress relief. *J. Mat. Sci.*, **25**(6) (1990) 2655–66.
4. Buessem, W. R., Cross, L. E. & Goswami, A. K., Effect of two-dimensional pressure on the permittivity of fine- and coarse-grained barium titanate. *J. Am. Ceram. Soc.*, **49**(1) (1966) 36–9.
5. Brown, R. F., Effect of two-dimensional mechanical stress on the dielectric properties of poled ceramic barium titanate and lead zirconate titanate. *Can. J. Phys.*, **39**(5) (1961) 741–53.
6. Ksendzov, Ya. M. & Rotenberg, B. A., The effect of pressure on the electric properties of barium titanate in weak fields. *Soviet Phys. Solid State (English Transl.)*, **1** (1959) 579–84.
7. Berlincourt, D. & Krueger, H. H. A., Domain processes in lead titanate zirconate and barium titanate ceramics. *J. Appl. Phys.*, **30**(11) (1959) 1804–10.
8. Kim, J.-J., Kim, B.-K., Song, B.-M., Kim, D.-Y. & Yoon, D. N., Effect of sintering atmosphere on isolated pores during the liquid-phase sintering of MgO–$CaMgSiO_4$. *J. Am. Ceram. Soc.*, **70**(10) (1987) 734–7.
9. Kulcsar, F., A microstructure study of barium titanate ceramics. *J. Am. Ceram. Soc.*, **39**(1) (1956) 13–17.
10. Diestelhorst, M., Hofmann, R. & Beige, H., Nonlinear properties of TGS- and $BaTiO_3$-crystals with defects. *Jap. J. Appl. Phys. Suppl.*, **24**(2) (1985) 1019–21.
11. Cook Jr, W. R., Domain twinning in barium titanate ceramics. *J. Am. Ceram. Soc.*, **39**(1) (1956) 17–19.
12. Arlt, G. & Sasko, P., Domain configuration and equilibrium size of domains in $BaTiO_3$ ceramics. *J. Appl. Phys.*, **51**(9) (1980) 4956–60.

13. DeVries, R. C. & Burke, J. E., Microstructure of barium titanate ceramics. *J. Am. Ceram. Soc.*, **40**(6) (1957) 200–6.
14. Arlt, G., Hennings, D. & de With, G., Dielectric properties of fine-grained barium titanate ceramics. *J. Appl. Phys.*, **58**(4) (1985) 1619–25.
15. Kaiser, D. L., Gayle, F. W., Roth, R. S. & Swartzendruber, L. J., Thermomechanical detwinning of superconducting $YBa_2Cu_3O_{7-x}$ single crystals. *J. Mater. Res.*, **4**(4) (1989) 745–7.
16. Chan, C. J., Lange, F. F., Rühle, M., Jue, J. F. & Virkar, A. V., Ferroelastic domain switching in tetragonal zirconia single crystals–microstructural aspects. *J. Am. Ceram. Soc.*, **74**(4) (1991) 807–13.
17. Ikegami, S. & Ueda, I., Mechanism of aging in polycrystalline $BaTiO_3$. *J. Phys. Soc. Jap.*, **22**(3) (1967) 725–34.
18. Schulze, W. A. & Ogino, K., Review of literature on aging of dielectrics. *Ferroelectrics*, **87** (1988) 361–77.
19. Cutter, I. A. & McPherson, R., Surface domain reorientation produced by abrasion and annealing of polycrystalline $BaTiO_3$. *J. Am. Ceram. Soc.*, **55**(7) (1972) 334–6.