

Direct Scanning Electron Microscopy Imaging of Ferroelectric Domains After Ion Milling

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A method for directly observing the ferroelectric domain structure by scanning electron microscopy after argon ion milling has been established. Its advantages are exemplified by exposing the domain structure in three widely used ferroelectric ceramics, BaTiO₃, (Na,K)NbO₃, and Pb(Ti,Zr)O₃. Stable high-resolution images revealing domains with widths <30 nm have been obtained. The domain contrast is caused by electron channeling and is strongly dependent on the sample tilt angle. Owing to a strain- and defect-free surface generated by gentle ion milling, pronounced orientation contrast is observed.

I. Introduction

TECHNIQUES to study the ferroelectric domain structure in bulk materials have been reviewed recently.¹ Among them there are a few examples of the application of scanning electron microscopes (SEM). Typically, ferroelectric domain structures are studied on etched samples. Etching creates topography on a previously polished surface due to the dependence of etching rates on domain orientation, first shown for BaTiO₃.² The resulting surface steps can then be imaged in light optical microscopes or SEM using secondary electrons. The major drawback of this method is that it is destructive, and *in situ* observations of the domain structure or of domain-switching phenomena are not possible. Furthermore, the etching conditions have to be optimized for each material, taking into account also the microstructure. In essence, each sample requires a customized etching procedure, the development of which may be tedious and time consuming.

In order to image the ferroelectric domain structures on uncoated, polished surfaces, low-voltage SEM techniques have been used to overcome excessive charging of the intrinsically isolating samples. Nevertheless, obtaining high-quality images at high resolution remains challenging. Several mechanisms for the origin of domain contrast have been proposed, e.g. different surface charging of antiparallel domains (polarization charges),^{3–7} the pyroelectric effect due to electron beam-induced heating, the inverse piezoelectric effect due to the electric field near the charged surface,⁸ or crystallographic orientation contrast due to electron channeling.⁹ Depending on the operating conditions of the SEM, different contrast mechanisms can be utilized to observe the domain structure.⁸

Horizontal orientation contrast imaging (using the backscattered electron [BSE] detector of an SEM) exploits the phenom-

enon of electron channeling¹⁰ to study the microstructures of metals and has been accepted as a standard method to determine the grain size.¹¹ For ceramics and other nonconducting materials, the technique is usually not well suited because it requires accelerating voltages above some 3 kV to detect BSEs as well as high probe currents. Still, orientation contrast is typically weak; therefore slow scan rates have to be used. All these factors render it challenging to obtain orientation contrast images from nonconductive samples before sample charging deteriorates the image quality. Furthermore, the surface layer of the material should be essentially free of strain and defects.⁹ A decade ago, the use of an environmental SEM (ESEM) to study ferroelectric domain structures was proposed.¹² In an ESEM, sample charging is avoided by observation under finite pressures. Surface charges are diverted by the chamber gas, e.g. water vapor, allowing for the observation of nonconducting samples. The authors reported that domain contrast could be seen on a polished surface after maximizing the probe current within the limits of the instrument used (highest accelerating voltage, largest condenser aperture, lowest condenser lens current), suggesting that domain contrast is caused by electron channeling.

In this communication, the use of argon ion milling as a preparation route for the study of ferroelectric domain structures is described. After ion milling, SEM observation is performed without coating the samples. The mechanism leading to the pronounced orientation contrast observed on essentially strain- and defect-free surfaces is discussed.

II. Experimental Procedure

The samples investigated in this study are dense bulk ferroelectric ceramics. Small pieces of the samples were glued onto Si wafers and embedded in two-component epoxy resin. Alternatively, prismatic blocks with approximate dimensions 5 mm × 5 mm × 1 mm were cut from bulk ceramics using diamond wafering blades. The samples were ground with 400 grit SiC paper. Then the prepolished surfaces were Ar ion milled for 12–15 h under an accelerating voltage of 5 kV and an ion beam current of 0.1 mA using a JEOL SM-09010 cross-section polisher (Jeol Ltd., Tokyo, Japan). By ion milling, an approximately 50- μ m-thick layer is removed from the mechanically prepolished surface, and an area of a few millimeter square of the underlying material is exposed without mechanical impact.^{13,14} Shorter ion-milling times of a few hours are applicable to achieve a slightly smaller polished area. The method is nondestructive; an ion-polished sample can be reused, e.g. for poling experiments or *in situ* observations of domain formation and switching. In the case of a fully dense sample, a flat surface can be obtained without etching of grain boundaries. However, if the sample contains pores, uneven surfaces topography originating from these pores are frequently observed, probably caused by the scattering of Ar ions at the pore edges. Nevertheless, grains in these uneven regions do not contain strain or extended defects as opposed to scratches on mechanically polished surfaces.

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SEM observations were performed using a JEOL JSM-7000F field-emission (FE) SEM or a JEOL JSM-820 SEM with W-filament gun. BSE images were recorded at scan rates of 40–120 s per frame. As long as the sample is not charging, the accelerating voltage has limited influence on contrast (at constant probe current), with the constraint that the BSE detector cannot detect electrons with energies lower than approximately 3 kV. On the other hand, contrast could be greatly enhanced by increasing the probe current, which essentially improves the signal-to-noise ratio. High quality images could be obtained with probe currents ≥ 1 nA. A compromise between contrast and image stability has to be made when the sample charges under the electron beam, i.e., images must be taken with lower probe current.

III. Results and Discussion

Figure 1 shows the microstructures taken on ion-polished surfaces of three ferroelectric ceramics, $(\text{Na,K})\text{NbO}_3$, BaTiO_3 , and $\text{Pb}(\text{Ti,Zr})\text{O}_3$, imaged using the BSE detector of a FE-SEM. Besides faceted grain structure, domains present inside individual grains are clearly visible in all samples with the narrowest one observed in $\text{Pb}(\text{Ti,Zr})\text{O}_3$ ceramics as indicated by arrows. It appears that the $(\text{Na,K})\text{NbO}_3$ and BaTiO_3 ceramics are fine-grained, with grain sizes of order $1 \mu\text{m}$ and domain widths of order 100 nm , whereas the $\text{Pb}(\text{Ti,Zr})\text{O}_3$ ceramics consists of even smaller grains and narrower domains, circa 200 and 30 nm , respectively. Obviously, it is hardly possible to study the microstructures and domain structures of these materials with an optical microscope. By argon ion milling, a strain- and defect-free surface layer can be obtained.¹³ Furthermore, sample charging is noticeably reduced after ion milling. The conditions of the sample after ion milling are therefore optimal for imaging grain orientation at a high probe current and low scan rates on a well-polished, flat surface.

Using a FE-SEM, it is possible to obtain BSE images at a high resolution, yet using a large beam current to maximize orientation contrast. The achievable resolution at the experimental conditions used in this study is estimated to be better than 10 nm . For comparison, an ion-polished sample of coarse-grained $(\text{Na,K})\text{NbO}_3$ ceramics with a grain size of order $10 \mu\text{m}$ has been studied with a W-filament SEM. Although inferior to the FE-SEM, pronounced orientation and domain contrast could be observed at sub-micrometer resolution.

The effect of specimen tilt on contrast is shown in Fig. 2. The contrast observed inside a single grain, i.e., domain contrast depends strongly on the orientation of the crystal. By tilting the sample $< 1.5^\circ$ (compare, e.g., images at 1.0° and 2.4° tilt angle), the pattern of bright and dark bands can be inverted, with hardly any contrast visible at an intermediate tilt angle. At the same time, the brightness of the central grain in Fig. 2 with respect to neighboring grains changes. At tilt angles $< 3^\circ$, the central grain appears darker than its surroundings whereas at angles $> 3^\circ$ it appears brighter. This pronounced angular contrast dependence is typical for orientation contrast images,^{9,13} suggesting that domain contrast is caused by electron channeling under these operating conditions of the SEM.

Ferroelectric domains in ceramics are formed by transformation-induced twinning when the material is cooled below the Curie temperature.¹⁵ Consequently, the unit cells in adjacent domains have a different crystallographic orientation, which gives rise to different intensities of BSEs due to electron channeling. For specific grain orientations, domain contrast becomes very strong and clear images of the domain structure can be obtained; a large difference in BSE intensity occurs when two adjacent domains are close to the Bragg condition. Because of the strict crystallographic orientation relationship and the small change in unit cell parameters accompanying the phase transition, two $90^\circ a-a$ or $a-c$ domains can be close to Bragg condition at almost the same angle with respect to the incident beam.¹⁵ If for one domain, the angle between the incident beam and the lattice planes is smaller than the Bragg angle,

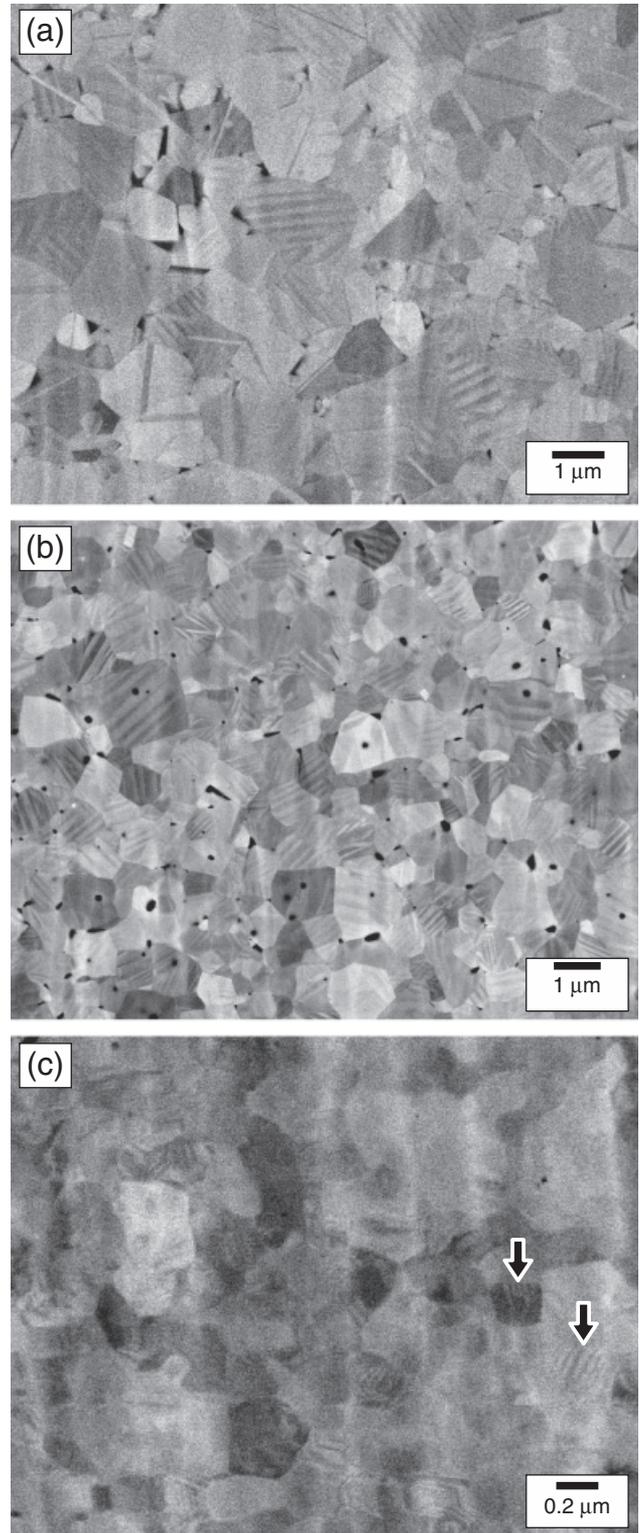


Fig. 1. Backscattered electron images revealing the microstructure features observed on ion polished surface of the $(\text{Na,K})\text{NbO}_3$ (a), BaTiO_3 (b), and $\text{Pb}(\text{Ti,Zr})\text{O}_3$ ceramics (c).

and for the other domain this angle is larger, the first domain appears bright whereas the second domain appears dark.¹⁰

IV. Conclusions

In conclusion, we have demonstrated the use of argon ion polishing for studying the domain structure of unetched, uncoated ferroelectric ceramics. Using the BSE detector of a FE-SEM, the image resolution is estimated to be better than 10 nm . Under these operating conditions of the SEM, domain contrast

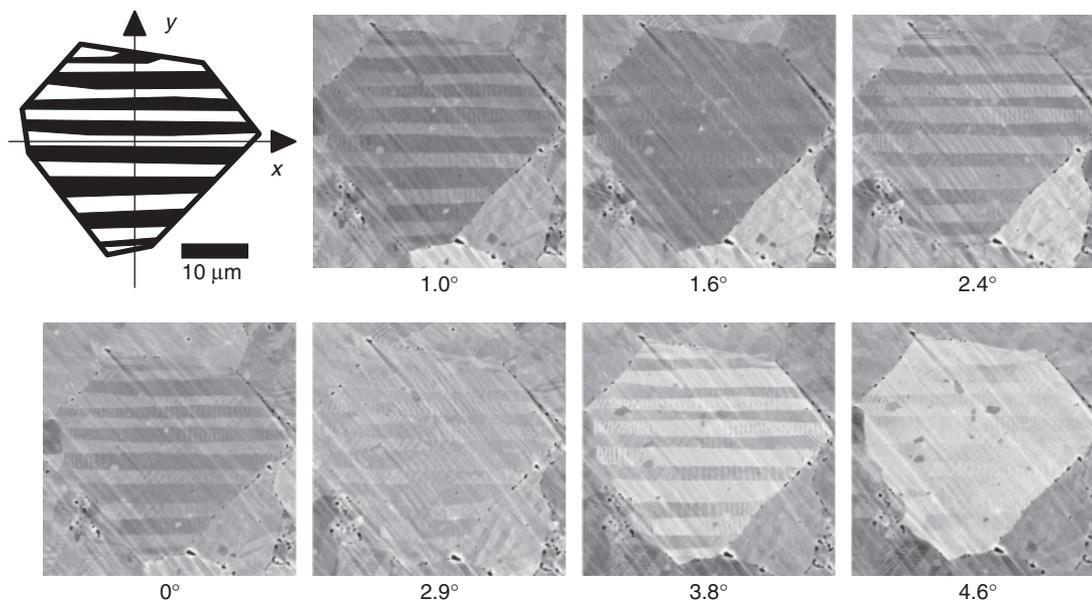


Fig. 2. Backscattered electron images of a grain in a coarse-grained (Na,K)NbO₃ sample at different tilt angles about the *y*-axis. Note the change in contrast inside the large, central grain and between the central grain and surrounding grains.

is confirmed to be caused by electron channeling. The technique presented in this study is particularly feasible for the study of polycrystalline materials with small grain sizes. Novel materials can be scanned for their ferroelectric domain structure rapidly without the need of developing chemical etching procedures. Microstructural features and ferroelectric domain structure can be extracted by one SEM observation. For typical bulk ceramics with grain sizes in the order of micrometers, the polished area contains several thousand grains; thus, microstructural data can be analyzed with statistical significance.

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