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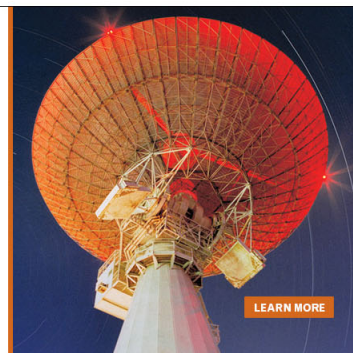
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Observation of partially incoherent $\langle 110 \rangle$ boundaries between polar nanodomains in $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ single crystals

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The ferroelectric domain structure of $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ single crystals was investigated by transmission electron microscopy (TEM) and piezoforce microscopy (PFM). Bright-field TEM and PFM images revealed the presence of polar nanodomains, whose boundaries had a tendency to align along the $\langle 110 \rangle$. High resolution TEM images revealed planar defects along these $\langle 110 \rangle$ boundaries, which partially relaxed the coherency of the lattice. © 2010 American Institute of Physics. [doi:10.1063/1.3488879]

I. INTRODUCTION

Recently, Pb-free piezoelectrics have attracted attention due to environmental concerns.^{1–3} $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ or NBT is an important lead-free ferroelectric (FE) with a high Curie temperature of $T_c \approx 320$ °C, a remnant polarization of $P_r = 38$ $\mu\text{C}/\text{cm}^2$, and a coercive field of $E_c = 73$ kV/cm.⁴ It has also been shown to have high piezoelectric properties of $d_{33} = 500$ pC/N, and thus to have the potential to replace the widely used lead-based piezoelectrics.^{2,5}

NBT has been reported to belong to the polar $R3c$ space group at room temperature.⁶ It is believed that NBT undergoes a phase transition sequence of high-temperature cubic (C) \rightarrow paraelectric tetragonal (T) \rightarrow FE rhombohedral (R) at temperatures of 520 °C and 250 °C, respectively.^{7–14} The T phase is ferroelastic, and there is no characteristic dielectric anomaly at the C \rightarrow T transition.^{15,16} Controversy remains concerning the T \rightarrow R transition. Neutron scattering and high resolution synchrotron x-ray diffraction have indicated a relatively wide transition range over which T and R phases coexist,^{11–13,17} whereas transmission electron microscopy (TEM) investigations of powder samples evidenced an intermediate modulated orthorhombic (O) phase that lies between the R and T phases in the temperature range between 230 and 300 °C.^{18,19}

An essential feature of all FEs is a polydomain structure. The formation of micrometric domains in NBT has been attributed to a deformation of the lattice along the $[111]$, which corresponds to the direction of the Bi shifting that produces a spontaneous polarization.²⁰ Prior studies of the domain structures of NBT have shown lamellar and needle-shaped morphologies.^{19,21} Furthermore, in the R $R3c$ phase, T platelets on the nanoscale have been reported.¹⁹ However, the findings do not help explain the relaxorlike characteristics in the R phase, as relaxors are characterized by polar nanodomains and the lack of normal long-range FE order. Re-

cently, temperature dependent domain studies of NBT by polarized light microscopy (PLM) have shown that T ferroelastic domains persist on cooling into the R phase field and by comparisons with piezoforce microscopy (PFM) images it was found that FE R nanodomains nucleate within the geometrical restrictions of the ferroelastic domains.²² These T domains are true (i.e., proper) ferroelastic domains and are not related to stress accommodation of the FE ones (i.e., improper). The persistence of the ferroelastic domains (formed under the condition of $c/a > 1$) into the R phase field (where $c/a \approx 1$) may complicate FE nanodomain nucleation.

Here, we have studied FE domains in NBT single crystals TEM and PFM. Both techniques demonstrated the presence of a polar nanodomain structure. High resolution TEM (HRTEM) image then revealed planar defects oriented along the $\{110\}$ boundaries between the nanodomains. Such planar defects interrupt lattice coherency, and will partially relax the elastic energy.

II. EXPERIMENT

Single crystals of NBT were grown by a top-seeded solution growth method. $\langle 001 \rangle$ oriented wafers of NBT single crystals were cut into dimensions of $3 \times 3 \times 0.5$ mm³ and the surfaces were polished down to a 0.3 μm finish. Careful investigations of the domain structure were performed by scanning probe microscopy using a piezoforce mode (Veeco DI 3100a): investigations were performed on crystals in the as-grown state. For TEM studies, single crystal specimens were cut in a $[001]$ orientation, which was then perpendicular to the direction of the electron beam. Specimens were prepared utilizing the standard techniques of grinding, dimpling, and argon ion-beam thinning (Model 1010 ion mill, E. A. Fischione Instrument, Inc., PA, USA). Bright-field TEM and selected area electron diffraction (SAED) studies were

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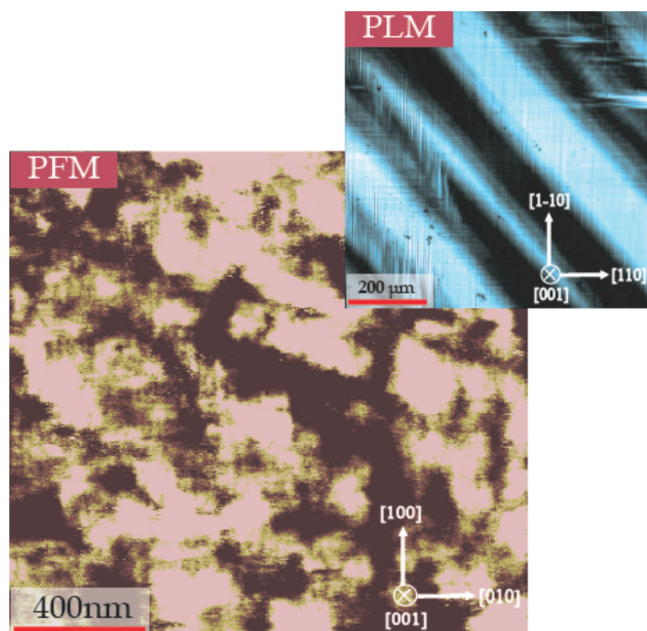


FIG. 1. (Color online) PFM image of the domain structures for NBT. The inset shows a corresponding PLM image.

performed using a Phillips EM-420 microscope operated at 120 kV. HRTEM experiments were performed using a FEI TitanTM TEM operated at 200 kV.

III. RESULTS

Figure 1 shows a typical PFM image of NBT taken in the R phase field at room temperature. This image clearly reveals the presence of nanosized polar regions, whose size was on the order of 200 to 500 nm. These polar nanoregions were not well organized but had some tendency for organization along the $\langle 110 \rangle$ direction as revealed by optical diffractograms obtained by fast Fourier transforms (FFTs). These findings are quite different from those of previous studies of NBT- x at. % BaTiO₃ for compositions close to the morphotropic phase boundary, where lamellar and needle-shaped domains have been reported.^{19,21} The inset in Fig. 1 shows a PLM image for NBT that reveals the presence of ferroelastic domains with a width of about 5–20 μm and a length on the order of hundreds of microns, and that were oriented along the $\langle 110 \rangle$. Temperature dependent studies (not shown, but can be found in Ref. 22) revealed that this ferroelastic domain structure remained present on heating until the T \rightarrow C phase boundary near ~ 520 $^{\circ}\text{C}$, which was far above the temperature of the dielectric constant maximum ($T_{\text{max}} = 320$ $^{\circ}\text{C}$). These results clearly demonstrate that the ferroelastic domains are not related to FE ones and those polar nanoregions nucleate within them on cooling into the R phase, as recently reported.²²

Next, a typical TEM bright-field image is shown in Fig. 2. This image also clearly reveals the presence of an extremely fine domain structure, which was characterized by a cross-hatched contrast. The features of this nanodomain structure are similar to that observed in the PFM image: except that the ones observed in the bright-field image were finer in size (50–100 nm), more wedge-shaped and had

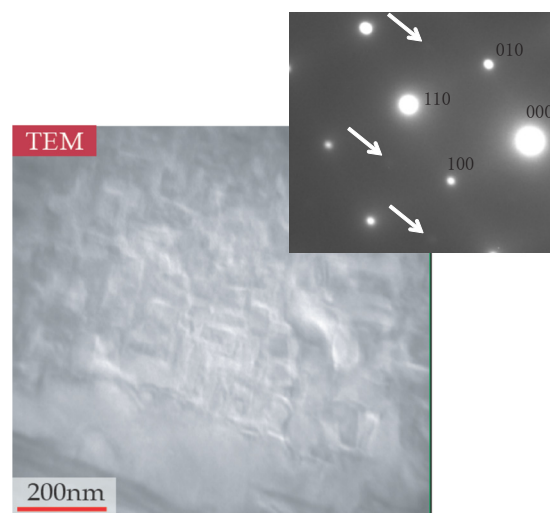


FIG. 2. (Color online) Bright-field TEM image of the domain structure for NBT. The inset shows a SAED pattern taken along the $\langle 001 \rangle$ zone.

boundaries with a much stronger tendency to align along $\langle 110 \rangle$. Comparisons of the bright-field and PFM images show that the nanodomain morphology observed by PFM was not as well-resolved as that in the bright-field image. Furthermore, the inset of Fig. 2 shows a $\langle 001 \rangle$ selected area diffraction pattern (SAED), where $(3/2 -1/2 0)$ and $(3/2 1/2 0)$ superlattice reflections are marked by arrows. These superlattice reflections could have intensity contributions from (i) oxygen octahedral tilts; (ii) chemical ordering of the A-site cations; and/or (iii) antiparallel displacements of cations.^{14,18,19,21,23–25} In fact, recent investigations^{18,21} have provided evidence that these superlattice reflections arise due to M-type oxygen octahedral rotations, typical of rotated T or O structures; rather than the R-type typical of a R one. Our observations, in the inset of Fig. 2, are consistent with this possibility.

The contrast in the bright-field image demonstrates a very fine polar nanodomain structure, with morphology similar to that of tweedlike structures in PMN- $x\%$ PT.²⁶ Such self-organization of polar nanodomains may occur to minimize stress, and to achieve the elastic compatibility conditions. Tweedlike structures are typically found in systems containing nanodomains which have local T lattice structures with a relatively high c/a ratio, such as for example premartensitic²⁷ and/or strain glass states.^{28,29} This observation is perplexing for NBT, as the structure is R ($a_r = 3.96$ \AA) with only a small R angle ($\alpha_r = 89.9^{\circ}$).¹⁶

To learn more about the polar nanodomains, we performed HRTEM studies. Figure 3(a) and 3(b) show a typical lattice image and its corresponding power spectrum (square of the magnitude of the complex Fourier transformation). This lattice image reveals polar nanodomains of about 50–100 nm in size, consistent with the bright-field image. In the lattice image, well-formed wedge-shaped boundaries between nanodomains can be seen that are oriented along $\langle 110 \rangle$. The well-defined orientation relation between the nanodomains is typical of that formed to relax the elastic energy of an invariant plane strain.^{28,29} However, some areas of the nanodomain boundaries oriented along the $\langle 110 \rangle$ consisted of

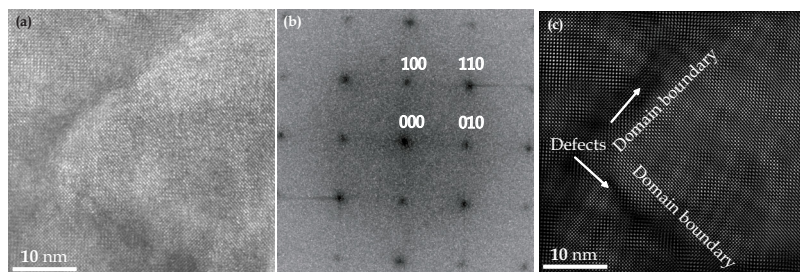


FIG. 3. (Color online) (a) Lattice image for NBT illustrating a boundary region between polar nanodomains; (b) power spectrum of image (a); and (c) an inverse fast Fourier-filtered image using a periodic (Bragg) filter.

planar defects. In order to better observe these features of the nanodomain structure, the lattice image was digitally filtered by selecting all the spots excluding the central spot in FFT using 1.5 nm^{-1} smooth edge masks and then taken inverse Fourier transformation which is presented in Fig. 3(c). This inverse FFT image clearly illustrates that the domain boundaries are delineated by these planar defects. Domain evolution seems to be limited by a pinning effect of domain boundaries by these defects.

IV. DISCUSSION

The elastic compatibility conditions of twinning relax the elastic energy while preserving the coherency of the lattice across the boundary. However, for NBT, it is important to note instead that the lattice coherence between the polar nanodomains in Fig. 3 was partially relaxed by planar defects. Some regions of the $\langle 110 \rangle$ boundaries were coherent, while others were incoherent. This indicates that the general geometrical invariant conditions cannot be achieved in the twinning process during polar nanodomain nucleation and growth and rather that the elastic energy is relaxed by partial incoherency of said boundaries.

The question must be asked as to why the general invariant conditions are not achieved for NBT, and why this might be important to its unique transformation mechanism. It is important to note that the structure of the stable phase at room temperature is R, which has a small c/a ratio. Generally, the boundaries between FE R domains are not strongly (improper) ferroelastic. However, the images in Figs. 1 and 2 demonstrated that the (R) polar nanodomains of NBT nucleated within the geometrical/elastic restrictions of a proper T ferroelastic domain structure (of notably larger size) that was inherited into the lower temperature R phase field. This persistence of the ferroelastic T domains into the R phase field undoubtedly complicates the $T \rightarrow R$ transformation, as there are no unique invariant conditions which can simultaneously achieve the elastic compatibility required for the simultaneous twinning of domains of both types of structures, which coexist one inside of another. Thus, the remaining way to reduce the excess elastic energy is to partially relax the coherency of the lattice itself across the boundary.

V. CONCLUSION

In summary, our investigations using electron and scanning probe microscopies have shown the presence of polar nanodomains in NBT single crystals. The polar nanodomains were shown to have a tendency to self-organize along the

$\langle 110 \rangle$. Studies by HRTEM revealed planar defects along these $\langle 110 \rangle$ boundaries, which reduced the elastic energy by partially relaxed the coherency of the lattice.

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