Transmission Electron Microscopy and Electron Diffraction Study on Nanodomain in Morphotropic Phase Boundary Ferroelectrics

Y. Sato[1], T. Hirayama[2], Y. Ikuhara[1,2]

[1]Institute of Engineering Innovation, The University of Tokyo, Tokyo, 113-8656, Japan
[2]Nanostructures Research Laboratory, Japan Fine Ceramics Center, Nagoya, 456-8587, Japan

A particular kinds of ferroelectric materials possess morphotropic phase boundary (MPB), which is the boundary between two different phases in the phase diagram. A typical example is the solid solution of PMN ($Pb(Mg_{1/3}Nb_{2/3})O_3$) and PT ($PbTiO_3$), PMN-PT. PMN-PT has MPB at the PT composition of about 30 %, and the single crystals of MPB composition exhibit very high piezoelectricity. The piezoelectricity is considered to be closely related with monoclinic crystal phase that appears in this particular compositional region. On the other hand, domain structure, which is characteristic to ferroelectric crystal, scales down to nano-meter level. This complicated situation makes it difficult to clarify the origin of piezoelectricity. To address this issue, we have characterized the crystalline structure of nanodomains [1]. In addition, response of nanodomains to external electric fields has been studied via *in-situ* transmission electron microscopy (TEM) [2,3]. In the present article, we briefly summarize these studies.

MPB PMN-PT crystal composes of hierarchical structure of microdomains and nanodomains (Fig. 1 (a)-(c)), where nanodomains are alternating twins of two different orientations. Selected area diffraction pattern taken from the microdomain *B* exhibits peak splitting, indicating that diffraction spots from two different nanodomain components (*c* and *d*) can be measured individually (Fig. 2 (a) and (b)). Close inspection reveals that the splitting patterns can be accounted for neither by tetragonal phase nor by rhombohedral phase, indicating that crystal structure of nanodomain should be explained as monoclinic phase [1].

On the other hand, our *in-situ* TEM studies have revealed that dominant process of the polarization reversal by the application of electric field is reorientation of nanodomains. The reorientation is reversal for the poled specimen [2] and irreversible for the unpoled specimen [3]. An example is shown in Fig. 3, where the nanoscale domain walls have the trace parallel to ($\bar{1}1\bar{1}$) before electrical biasing and the trace becomes parallel to (001) under an electric field along [001] (Ref. 3). In terms of permissible domain walls in a monoclinic (*Pm*) phase [4], ($\bar{1}1\bar{1}$) and (001) domain walls may be characterized as S_1-type and W_f-type domain walls. Thus, monoclinic nanodomain scenario can well account for the crystal phase and the response of nanodomains in MPB PMN-PT.

References
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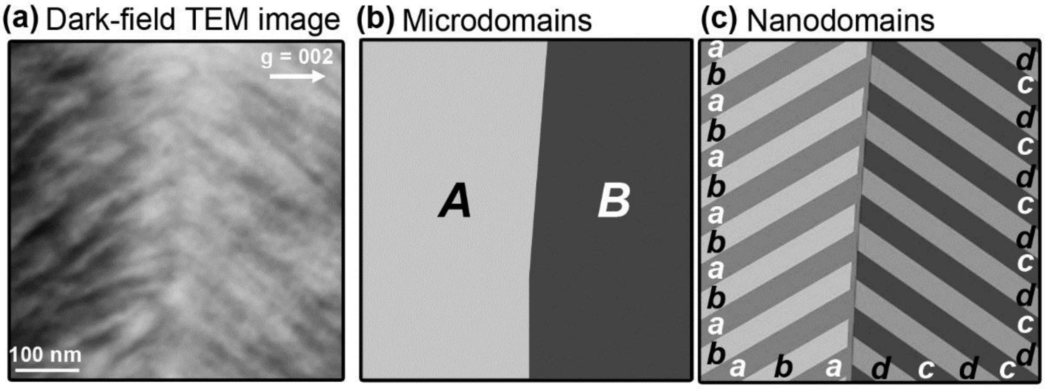

FIG. 1. (a) Dark-field TEM image of a MPB PMN-PT single crystal and schematics of (b) the microdomains (*A* and *B*) and (c) the nanodomains (*a* - *d*). [1]

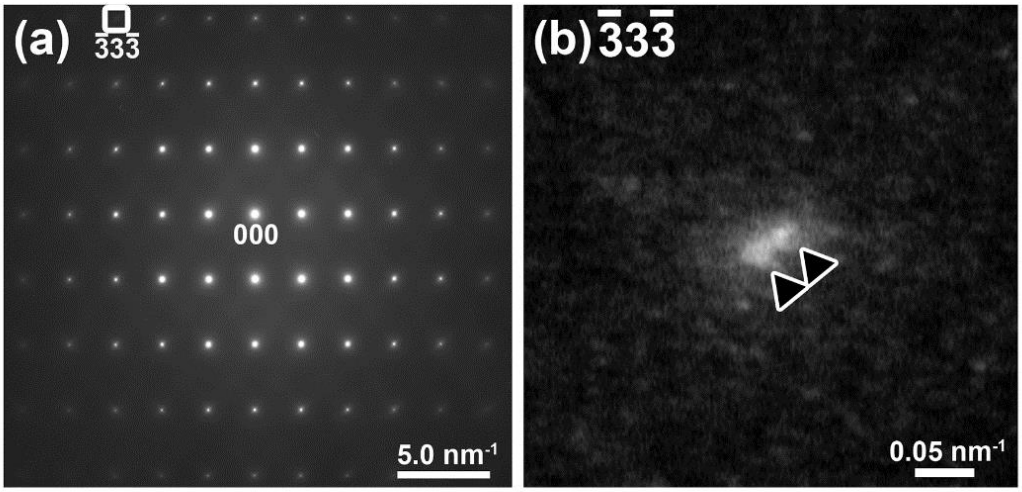

FIG. 2. (a) Selected area diffraction pattern taken from a MPB PMN-PT single crystal with the zone axis of [$\bar{1}\,\bar{1}\,0$]. (b) Enlargement of the $\bar{3}3\bar{3}$ spot, which exhibits the splitting into two. [1]

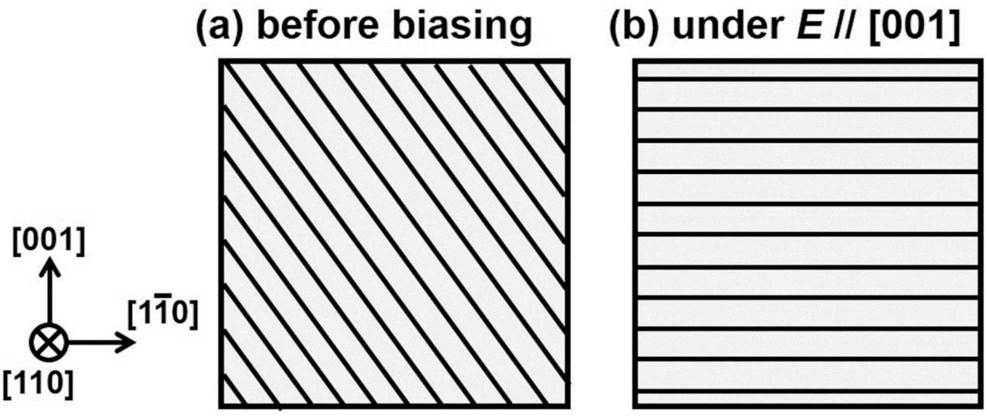

FIG. 3. Domain structure in a MPB PMN-PT single crystal (a) before electrical biasing and under an electric field of ~ 10.8 kV/cm along [001]. The schematics are drawn based on the results in Ref. 3.