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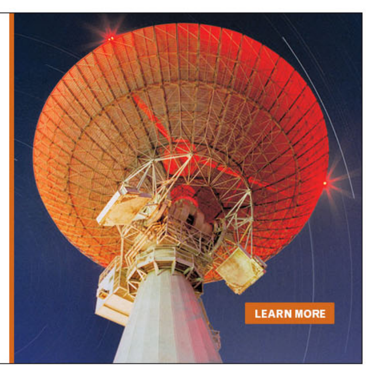

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Domain structure changes in $(1\text{-}x)Pb(Mg_{1/3}Nb_{2/3})O_3\text{-}xPbTiO_3$ with composition, dc bias, and ac field

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Domain structure changes in $(1\text{-}x)Pb(Mg_{1/3}Nb_{2/3})O_3\text{-}xPbTiO_3$ have been studied by polarized optical microscopy. In the zero-field-cooled condition, increasing the x revealed systematic changes in the domain morphology from polar nanodomains for $x<0.25$, to fine crosshatched domains near the morphotrophic phase boundary (MPB), and to micro-sized domains for $x=0.4$. In the vicinity of the MPB, an applied dc electrical bias resulted in a change of morphology from fine crosshatched (rhombohedral phase) to thin-aligned striationlike (monoclinic phase) domains. The application of an ac electric field to the crosshatched domains resulted in irregular domain wall oscillations/relaxations and increased nonuniformity. ©2004 American Institute of Physics. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1779971]

The crystalline solution $(1\text{-}x)Pb(Mg_{1/3}Nb_{2/3})O_3$ $\text{-}xPbTiO_3$ (PMN-xPT) is known to have complex structure-property relationships. In the unpoled condition for $x<0.35$, a relax or a ferroelectric state is known to exist, characterized by a frequency-dispersive dielectric maximum[1,2] and a polarization freezing into a glasslike condition at lower temperature.[3] The x-ray-diffraction (XRD) and the neutron-diffraction investigations have shown a tetragonal-ferroelectric (FE_t) phase for $x>0.35$, a rhombohedral-ferroelectric (FE_r) phase for $0.25\approx x<0.35$,[4,5] and a slightly distorted pseudocubic phase designated as X for $x<0.25$.[5–7] Previous transmission electron microscopy (TEM) studies[8–10] revealed polar nanodomains (PND) of several hundred angstroms in size for $x<0.3$, where the average size decreases with decreasing x; small crosshatched tweedlike domains for $0.3\approx x<0.35$; and normal micron-sized 90-degree domains in the FE_t region. Also, polarized light microscopy (PLM) studies have revealed a contrast on a length scale much smaller than that of the wavelength of light in the FE_r and X-phase regions,[11] which is indicative of the PND; an intimate mixture of small FE_r and FE_t domains near the morphotropic phase boundary (MPB);[12] and micron-sized 90-degree domains in the FE_t region.[12]

In contrast, for $0.2\approx x<0.35$, crystals of PMN-xPT poled along (001) exhibit extremely high electromechanical properties.[13,14] The XRD and the neutron-diffraction investigations[4,15] have revealed a monoclinic M_a phase for $0.2\approx x<0.3$ and a monoclinic M_c phase for $0.3<x<0.35$. Prior TEM studies of PMN-35PT have shown that thin-domain striations can be induced from the tweedlike domains by increasing the electron beam intensity.[10,16] In addition, recent polarized optical microscopy studies of PMN-33PT crystals revealed similar thin-domain striations,[17] where analysis of the thin striations by various optical conditions indicated that they are monoclinic M_c domains.

The purpose of this investigation was to study the changes in the domain structure with composition, dc bias, and ac field for (001)-oriented PMN-xPT crystals by polarized optical microscopy. Investigations have focused on revealing how the domain structure changes (i) with increasing x between phase X, FE_r, and FE_t in the zero-field-cooled (ZFC) condition, (ii) from the FE_r phase in the ZFC condition to the M_a phase in the poled one, and (iii) with increasing ac field.

Polarized optical microscopy studies were performed on a (001)-oriented PMN-xPT crystals of nominal compositions of $x=0.13$, 0.3, and 0.4. The crystals for the study were provided by the Institute of Physics at Rostov State University. They were grown by spontaneous crystallization from a solution melt. The specimens were cut into plates with typical dimensions of $4\times4\times0.1$ mm^3. All faces of the crystal were polished to a 0.1 μm finish. Two thin-gold electrodes were then deposited on the same face of the crystal via sputtering through a mask. The domain morphologies were then observed as a function of the field between these electrodes. The normal to the face, on which the electrode was deposited (used to apply an electric field), is designated as (001) or the c axis. Before the measurements were begun, the crystals were annealed. Careful investigations were performed using the polarized optical microscopy, starting from the annealed condition. Domain morphologies were characterized by a Leica polarized light microscope. Domain structures were observed between a crossed polarizer-analyzer setting along the (001) using a quarter-wave plate.

Figure 1 shows the PLM images taken in the ZFC condition of a (001)-oriented PMN-xPT for (a) $x=0.13$, (b) $x=0.3$, and (c) $x=0.4$. At low PT contents, the domain morphology consisted of a very fine mottled interference pattern, consistent with the previous TEM studies, which revealed the PND.[8–10] The images were taken from relatively thick

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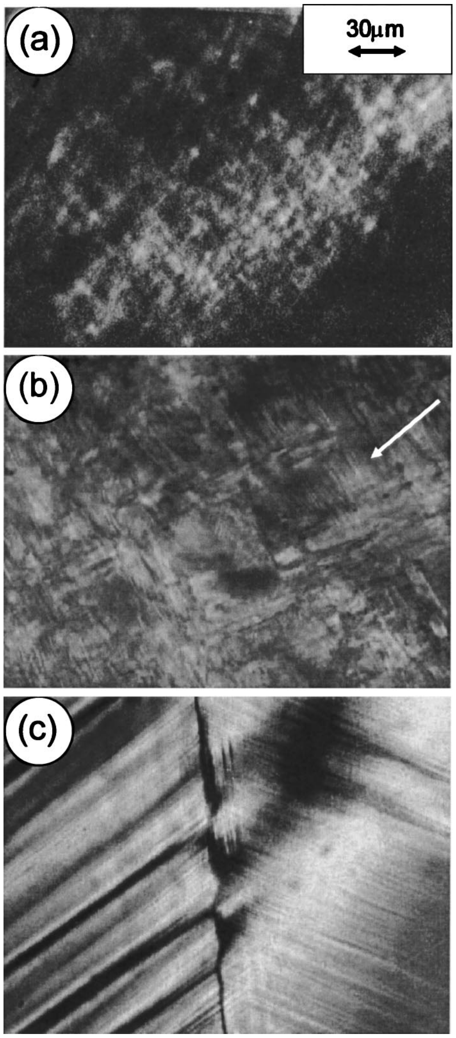

FIG. 1. Polarized optical micrographs for various (001)-oriented PMN-xPT crystals (a) $x=0.13$, (b) $x=0.3$, and (c) $x=0.4$. These data were taken in a zero-field-cooled condition.

specimens (0.1 mm), indicating that such miniature domains constitute the sample volume and are not a surface artifact. Comparisons of the results with the diffraction studies[5–7] indicate that phase X consists of miniature polar domains (PND), which do not self-assemble into twin bands in order to achieve an elastic compatibility.[18–22] With increasing PT content, the miniature polar domains exhibited increasing degrees of self-organization, as illustrated in Fig. 1(b) for $x=0.3$. This figure shows the miniature striationlike domains that are crosshatched. The $\{110\}_c$ twin walls are present, indicated by an arrow, which are somewhat blurred. Comparisons with the diffraction studies[4,5] indicate the phase R consists of miniature domains that are assembled in small patches, suggesting the onset of a twin-band formation. At higher PT contents of $x>0.35$, the micron-sized 90° domains were found, as shown in Fig. 1(c). Comparisons with the XRD studies[4] indicate that the micron-sized 90-degree domains in the FE_t phase are well organized into polydomain twin bands (plates), which are in turn arranged to fill the specimen, achieving full-stress accommodation typical of martensite.[18–22]

Figure 2 shows the PLM images for a (001)-oriented PMN-30PT taken in (a) the ZFC condition and (b) under a dc bias of $E_{dc}=10$ kV/cm, which is sufficient to achieve a fully poled state. Application of a dc bias did not result in significant changes in the domain size, as the miniature domains of approximately the same size can be seen in both figures. However, the domain morphology is notably altered—the small crosshatched domains of the ZFC condition are changed into fine striationlike domains that exhibit a significant degree of a alignment along $\{110\}_c$. Comparison with the prior diffraction studies[4,5,15] indicates that the M_a phase consists of miniature domain striations that are well organized into twin bands, filling the specimen volume; whereas the FE_r phase consist of the miniature domains partially organized in a crosshatched or patched manner, as discussed earlier. Domain self-organization is driven by an elastic compatibility. The domain morphologies of Fig. 2 indicate that the M_a phase has achieved a significantly higher degree of stress accommodation, relative to that of the FE_r. This is consistent with the diffraction studies, which have shown that the M_a phase has significantly less line broadening than the FE_r.[23,24]

Figure 3 shows a PLM image for a (001)-oriented PMN-30PT taken under an ac electric field of $E_{ac}=2$ kV/cm, which had initially been in a ZFC condition, Significant changes in the image were found under the ac drive, relative to that for $E=0$ kV/cm, as given in Fig. 2(a). The domain morphology for $E_{ac}=2$ kV/cm can be seen to (i) exhibit significant color contrast, (ii) to be quite nonuniform, and (iii) to contain fine contrast, illustrated in the circular region. The color contrast under the increasing ac drive reveals that the optical activity of the crystal is spatially nonuniform

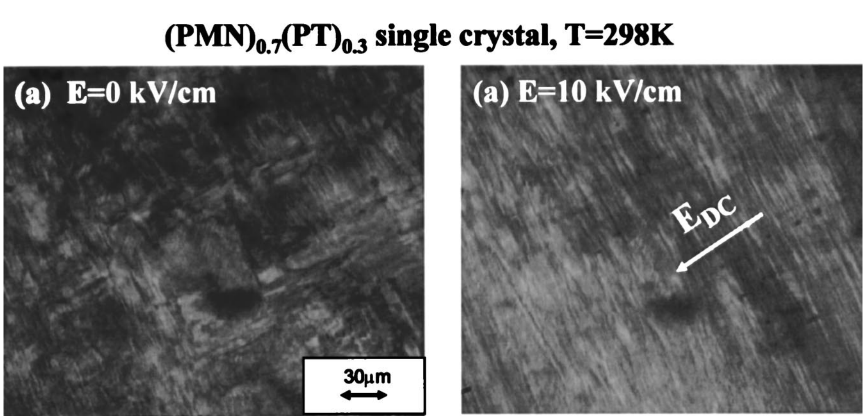

FIG. 2. Polarized optical micrographs of a (001)-oriented PMN-30PT crystals for various electrical histories (a) in the zero-field-cooled condition and (b) under a dc electrical bias of $E=10$ kV/cm.

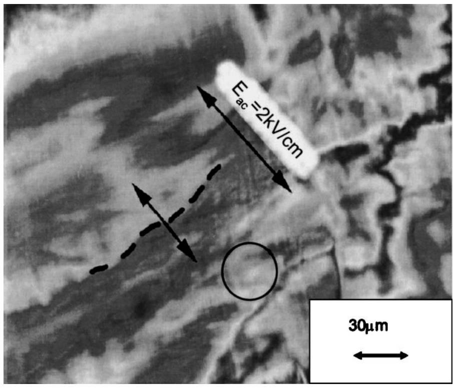

FIG. 3. Polarized optical micrograph of a (001)-oriented PMN-30PT crystal under an ac electrical field of $E=2$ kV/cm. Investigations were begun from the zero-field-cooled condition.

throughout the crystal. Underlying this nonuniformity is an enhanced domain heterogeneity. Under an ac electric field, the organization of the miniature domains into the patches of Fig. 2(a) is broken down, resulting in the stabilization of smaller scale features that are similar to those observed at the lower PT contents [see Fig. 1(a)]. The change in the domain morphology between the FE_r and the M_a phases does not occur by a gradual alignment of the miniature domains but rather by the destruction of the patchlike patterns, in which the miniature domains are organized in the FE_r phase and presumably the subsequent self-organization of the miniature domains into a well-aligned striation pattern in the M_a phase. In addition, under the low-frequency ac drive, the color contrast oscillated. The oscillations are illustrated in Fig. 3, as indicated by an arrow. The changes in the PLM images with an ac electric field are consistent with the polarization switching by a heterogeneous nucleation, where the nucleation sites are not restricted to pre-existing domain boundaries, but can occur throughout the volume of the material in the vicinity of random fields.[26,27]

In summary, the polarized optical microscopy studies of the PMN-xPT have shown (i) the miniature polar domains that exhibit an increasing degree of self-assembly with increasing x, (ii) that the $FE_r \rightarrow M_a$ transition induced under dc bias results in a change between the miniature crosshatched domains and the fine well-aligned striation domains, and (iii) that an ac electric field applied to the crosshatched domains result in irregular domain wall oscillations/relaxations.

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