Response of polar nanoregions in 68%Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-32%PbTiO$_3$ to a [001] electric field

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We report neutron diffuse scattering measurements on a single crystal of 68%Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-32%PbTiO$_3$. Strong diffuse scattering is observed at low temperatures. An external field applied along the [001] direction affects the diffuse scattering in the (HK0) plane significantly, suggesting a redistribution occurs between polar nanoregions of different polarizations perpendicular to the field. By contrast, the [001] field has no effect on the diffuse scattering in the ($H0L$) and ($0KL$) zones. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2959077]

The complex perovskites $(1-x)$Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-xPbTiO$_3$ (PMN-xPT) and $(1-x)$Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-xPbTiO$_3$ (PZN-xPT) are of great interest because of their promising piezoelectric properties.[1–3] They are prototypical ferroelectric relaxors (relaxors hereafter) that have large and strongly frequency-dependent dielectric constants, which peak broadly in temperature.[1,4] A unique property of relaxors is the existence of polar nanoregions (PNRs), a concept first proposed by Burns and Dacol in 1983.[5] The PNRs start to form on cooling at the "Burns temperature" T_d, continue to grow with decreasing temperature, and can be directly probed by neutron/x-ray.[6–13]

Recent work on PZN-4.5%PT suggests a close connection between PNRs and the ultrahigh piezoelectric response in relaxors.[14] Previous studies have confirmed that diffuse scattering from PNRs disappears for compositions on the ferroelectric side of the phase diagram,[15,16] while the integrated diffuse scattering intensity appears to reach a maximum near the morphotropic phase boundary (MPB).[15] The application of an external field along [111] redistributes the PNRs, resulting in a change in the diffuse scattering patterns;[14,17,18] however, the effect of external field along [001] is not yet fully understood.[19] To understand the role PNRs play in the piezoelectric response of relaxor systems, we believe it is now becoming more important to understand how they behave within the MPB region where the piezoelectric properties are optimal in both PMN-xPT and PZN-xPT,[20–22] and in particular how they respond to an external field along [001], which is the poling direction that produces the greatest piezoelectric effect.

In this letter, we present neutron scattering results on a PMN-32%PT single crystal, a composition that lies inside the MPB. Our results show that (i) there is strong diffuse scattering in this compound with a spatial distribution similar to that observed in other PMN-xPT and PZN-xPT systems,[9,10,12,13,23,24] (ii) the diffuse scattering in the (HK0)

plane responds to a moderate external field ($E=2$ kV/cm) applied along [001], which is probably associated with low symmetry local structures induced by the field and internal strain in the compound, and (iii) the field does not affect the diffuse scattering in the ($H0L$) and ($0KL$) zones.

The crystal has a rectangular shape, dimensions of 10 $\times$10$\times$2 mm^3 with six {100} surfaces, and was provided by TRS Ceramic. Neutron scattering experiments were carried out on the triple-axis spectrometer BT9 located at the NIST Center for Neutron Research (NCNR) using beam collimations of 40′-40′-S-40′-80′ (S=sample) with fixed initial and final neutron energy of 14.7 meV. An electric field of 2 kV/cm was applied along [001] during field-cooled (FC) measurements.

In Figs. 1(a) and 1(b), the (300) Bragg peak longitudinal full width at half maximum (FWHM) and intensity are plotted. Two phase transitions occur at $T_{C1}\sim430$ K [cubic (C) to tetragonal (T)] and $T_{C2}\sim355$ K [T to monoclinic (M)]. These results are consistent with previous results,[25–27] and confirm that the composition of the sample lies inside the MPB.

In our PMN-32%PT sample, we observed strong diffuse scattering, which increases monotonically with cooling as demonstrated in Fig. 1(c). In Figs. 2(a) and 2(b), we show selected linear scans offset from the (300), (003), (200), and (002) Bragg peaks in the ($H0L$) plane under zero-field-cooled (ZFC) and FC conditions at 200 K. When we compare ZFC and FC results, it is clear that in the ($H0L$) zone, a [001] field has no detectable effect on the diffuse scattering. Based on earlier models,[23] we suggest that in this compound PNRs with polarizations not perpendicular to the [001] field (in this case, [101], [011], [$\bar{1}$01], and [$0\bar{1}$1]) are not affected.

Figures 2(c) and 2(d) show similar linear scans of the diffuse scattering measured near (200) and (300) at different temperatures in the (HK0) zone, where the [001] electric field is now perpendicular to the scattering plane. Here, the FC and ZFC data now show clear differences. When ZFC at 200 K, the diffuse scattering exhibits a symmetric double-peaked profile for both $(2.9,K,0)$ and $(2.1,K,0)$ scans.

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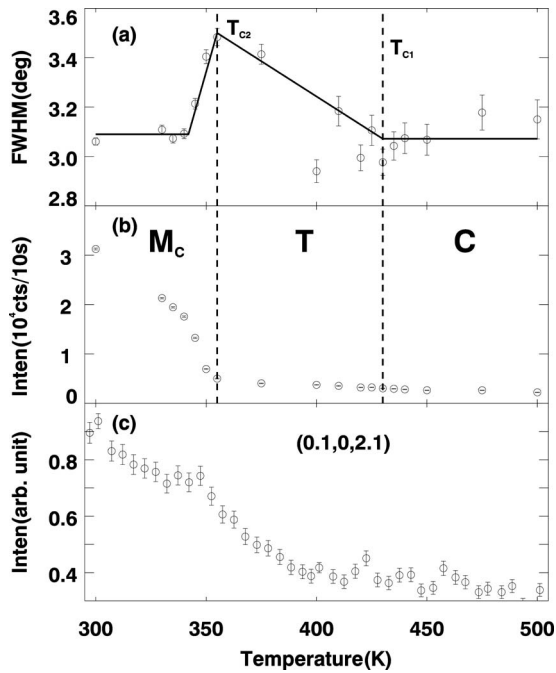
FIG. 1. Temperature dependence of the (a) (300) peak longitudinal FWHM, (b) (300) peak intensity, and (c) diffuse scattering intensity at (0.1,0,2.1). Solid lines are guides to the eye. Dashed lines indicate the phase transition temperatures. Error bars in (a) are obtained by least-square fitting the data with Gaussian functions, and those in (b) and (c) represent the square root of the counts. The bump in (c) at ∼355 K is due to critical scattering.

When FC at $T \gtrsim 400$ K, where the diffuse scattering is still weak, the field effect is not apparent and the diffuse scattering remains symmetric in shape; at lower temperatures the diffuse scattering becomes more intense, and the diffuse profile becomes asymmetric.
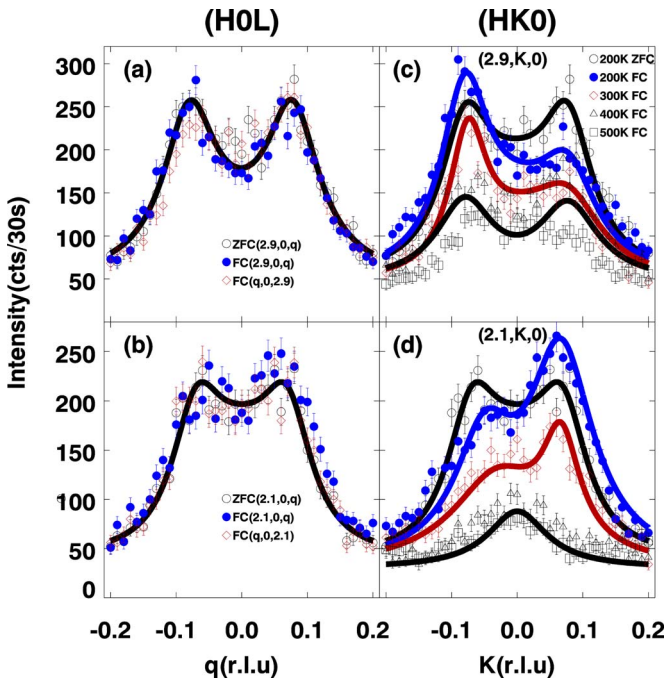

FIG. 2. (Color online) Linear scans of the diffuse scattering intensity measured in the (H0L) plane at 200 K around (a) (300) (ZFC, open circles and FC, closed circles) and (003) (FC diamonds); (b) (200) (ZFC, open circles and FC, filled circles) and (002) (FC, diamonds). (c) and (d) are linear scans of the diffuse scattering along $(2.9, K, 0)$ and $(2.1, K, 0)$ at different temperatures in the (HK0) plane. Lines are guides to the eye. Error bars represent the square root of the counts.
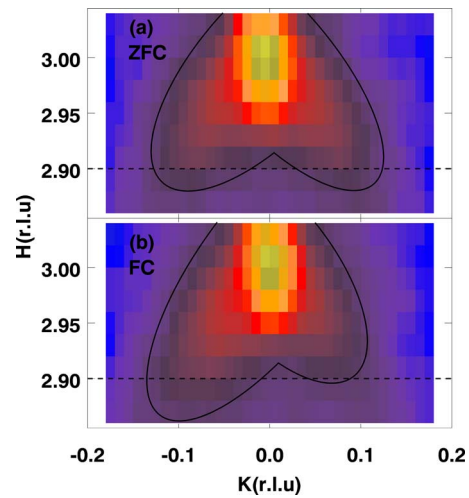

FIG. 3. (Color online) Contour maps of diffuse scattering around (300) at 200 K, (a) ZFC, (b) FC. Solid lines are guides to the eye. Dashed lines indicate the scans in Fig. 2(c) at 200 K.

These features can be more clearly seen in the diffuse scattering contour maps in Fig. 3. Figure 3(a) shows that at 200 K, under ZFC conditions, there is strong diffuse scattering having a symmetric butterfly shape with one wing along [110] and the other along [$\bar{1}$10], centered at (300). We are only able to measure the bottom part of this butterfly because of mechanical restrictions on the Q range. Under FC conditions, some intensity from the wing along [$\bar{1}$10] is shifted to the other wing along [110], creating the asymmetry.

We have performed multiple FC sequences and these results are reproducible. Also note that the change in diffuse scattering in the (HK0) plane persists even after the removal of the external field below T_C. Only by heating the sample to high temperature (500 K) and cooling in zero field can one remove the field effect. This is similar to that measured in PZN-*x*PT samples,[17,28] where the change of the diffuse scattering is believed to be associated with the formation and change of ferroelectric domains. However, there are some differences between the effect of external field along [001] and [111] in that, (i) a [001] field only affects some of the PNRs (those with polarizations in the (H0L) and (0KL) planes are not affected), and (ii) the magnitude of the redistribution (enhancement/suppression) is smaller for a [001] field compared to that for a [111] field. To understand the effect of domain change on the PNRs, one needs to take into consideration the low temperature structure of PMN-32%PT. Previous x-ray diffraction work suggests that the system enters a monoclinic-C (M_C) phase when cooled under a [001] field.[26] Under ZFC conditions, any domain effect will be averaged over the multidomain state. On the other hand, when cooled under a field along [001], the domain structure becomes more organized, where (it is believed that) the c^* is fixed along the field direction. Our results suggest that PNRs with [101], [011], [$\bar{1}$01], and [0$\bar{1}$1] polarizations are not affected when the phase transition into this c^* fixed monoclinic domain state occurs, whereas those PNRs with [110] and [1$\bar{1}$0] polarizations are affected.

In an M_C phase, either the cubic a axis or cubic b axis is tilted up/down toward the c axis. In a perfect system, one would have equal numbers of all four different M_C domains (see Fig. 2 in Ref. 29). In reality, this may not be the case due

to external/internal strains, growth conditions, etc. Nevertheless, the asymmetric butterfly-shaped diffuse scattering suggests that in this c^* fixed M_C phase, there are more PNRs with $[1\bar{1}0]$ polarizations (which yield diffuse scattering along the $[110]$ direction) than those with $[110]$ polarizations. This apparently cannot be naively explained by any distribution of c^* fixed M_C domains, since $[110]$ and $[1\bar{1}0]$ directions are equivalent in any of the four M_C domains. Our speculation is that the true (local) symmetry of these M_C domains could be even lower (e.g., triclinic), as predicted by Vanderbilt and Cohen using higher-order Devonshire theory,[30] so that $[110]$ and $[1\bar{1}0]$ directions are different in these domains and a preference for PNRs with these polarizations within each domain is realized, and observed when ferroelectric domain distribution changes.

In summary, we have performed neutron diffuse scattering measurements on a PMN-32%PT single crystal under ZFC and FC conditions. It is shown that strongly anisotropic diffuse scattering exists, which increases monotonically with cooling. These results suggest that PNRs do exist and behave very similarly for this composition inside the MPB region compared to those on the left side (relaxor side) of the PT doping phase diagram previously studied. The shape of the diffuse scattering can be modified by an external field of moderate strength along $[001]$. The true nature of this field effect on the PNRs is not yet fully understood, but we conjecture that it might be related to the formation/redistribution of ferroelectric domains having a symmetry even lower than monoclinic, in which the PNRs reside.

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