PHYSICAL REVIEW B **79**, 052101 (2009)

Temperature evolution of short- and medium-range ionic correlations in relaxor ferroelectric $[\mathrm{Pb}(\mathrm{Zn}_{1/3}\mathrm{Nb}_{2/3})\mathrm{O}_3]_{1-x}[\mathrm{PbTiO}_3]_x$ ($x=0.05$, 0.12)

I.-K. Jeong*

Department of Physics Education and Research Center for Dielectrics and Advanced Matter Physics, Pusan National University, Busan, 609-735, Korea

and Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

(Received 27 October 2008; revised manuscript received 6 January 2009; published 9 February 2009)

We performed temperature-dependent neutron pair distribution function (PDF) analysis on relaxor ferroelectric $[\mathrm{Pb}(\mathrm{Zn}_{1/3}\mathrm{Nb}_{2/3})\mathrm{O}_3]_{1-x}[\mathrm{PbTiO}_3]_x$ (PZN-xPT) ($x=0.05$ and 0.12) from 550 to 150 K. The experimental PDF spectra clearly demonstrate that PZN-5%PT and PZN-12%PT have basically same ionic pair correlations up to the pair distance $r\sim 15$ Å at all temperatures despite their difference in low-temperature long-range crystal structures. At longer pair distances $30<r<50$ Å, however, ionic pair correlations of PZN-5%PT and PZN-12%PT gradually diverge from each other below $T\sim 450$ K. Based on these PDF results, we propose that a distinct ordering of polar nanoregions develops between PZN-5%PT and PZN-12%PT with decreasing temperature.

DOI: 10.1103/PhysRevB.79.052101 PACS number(s): 77.84.Dy, 61.05.fm, 61.43.Gt, 61.50.Ks

Polar nanoregions (PNRs) are a central ingredient of relaxor ferroelectrics which are characterized by a broad temperature-dependent permittivity as well as a strong frequency dispersion.[1,2] Thus, many experimental and theoretical studies have been performed to understand microscopic origins[3–5] as well as static and dynamic behaviors[6–15] of PNRs under various external environments such as temperature, electric field, and pressure. The formation of PNRs was first proposed by Burns and Dacol[16] to interpret the deviation of index of refraction of $\mathrm{Pb}(\mathrm{Mg}_{1/3}\mathrm{Nb}_{2/3})\mathrm{O}_3$ (PMN) from a linear temperature dependence below the so-called Burns temperature T_B. Below the Burns temperature, both correlation length ξ and the volume fraction α of PNRs are known to increase with decreasing temperature. In PMN, for example, ξ increases from ~ 15 Å at 500 K to ~ 60 Å at 10 K (Ref. 17) and α up to 30% at 15 K.[10,18] These results suggest that reorientable PNRs merge together with decreasing temperature and eventually freeze in a disordered lattice.[19]

Recently, interesting experimental results were reported on the response of PNRs under an external electric field applied along the [111] direction. In $\mathrm{Pb}(\mathrm{Zn}_{1/3}\mathrm{Nb}_{2/3})\mathrm{O}_3$ (PZN), it is observed that PNRs do not align with the external field of up to 40 kV/cm but redistribute among six equivalent directions.[11] In addition, PNRs in PMN-28%PT are found to rotate toward the four $[1\pm 11]$ and $[11\pm 1]$ directions with equal probability to produce a net polarization along the [100] field direction.[20] Similar order-disorder behavior of PNRs was proposed in PZN-xPT at 15 K as a function of PbTiO_3 concentration without external electric field.[21] This redistribution or ordering of PNRs under external stimuli may induce strain and is thus expected to play a role in the electromechanical response of relaxor ferroelectrics.

In this Brief Report we report an order-disorder behavior of PNRs in PZN-5%PT and PZN-12%PT. PZN-xPT has a long-range cubic structure at high temperatures. As the temperature decreases, the system undergoes a phase transition to rhombohedral ($x\leq 8\%$), orthorhombic ($8\%<x<11\%$), and tetragonal ($x>11\%$) structures depending on the PbTiO_3 concentration.[22] PZN-5%PT and PZN-12%PT are located at the left and right sides of the morphotropic phase boundary which separates the rhombohedral and tetragonal regions.[23] To study the ordering of PNRs across long-range phase transition, we used neutron pair distribution function (PDF) analysis as a function of temperature from 550 to 150 K. The PDF spectrum[24] is a real-space representation of atomic-pair distances and can be obtained from powder-diffraction data using the following equation: $G(r)=4\pi r[\rho(r)-\rho_0]=\frac{2}{\pi}\int_0^{Q_{\max}}Q[S(Q)-1]\sin Qr\,dQ$. Here, r represents the atomic-pair distance, $\rho(r)$ is the atomic-pair density, ρ_0 is the average pair density, and Q is a magnitude of a scattering vector. The total scattering structure function $S(Q)$ is a normalized powder-diffraction intensity which includes both diffuse scattering and Bragg peaks. The resultant PDF spectrum provides information on short-, medium-, and long-range crystal structure and thus has been used to study complex crystal structures of relaxor ferroelectrics.[25] The experiments were performed on the NPDF instrument at the Los Alamos Neutron Science Center. For data reduction, the PDFGETN program is used.[26]

We first discuss the long-range crystal structures. Figure 1 shows a selected Bragg peaks for PZN-5%PT and PZN-12%PT at 550 and 150 K. Consistent with earlier experiments,[22] the evolution of Bragg peaks at the low temperature indicates that high-temperature cubic structure undergoes phase transitions to rhombohedral and tetragonal structures, respectively. Solid lines are fittings obtained from Rietveld refinements using GSAS (Ref. 27) and EXPGUI.[28] Table I summarizes atomic parameters of PZN-5%PT and PZN-12%PT at 150 K obtained from Rietveld refinements. Here we note that the thermal parameter of Pb ion is extraordinarily large, being about 10 times that of the Zn/Nb/Ti. Similar results were reported by other authors as well.[29,30] This huge Pb thermal parameter is strong indicative of large structural disorder on Pb site. Regarding the origin of the Pb-site disorder, first-principles calculations on PMN show that Pb ions are displaced away from high-valence cube faces toward lower-valence cube faces; i.e., Pb ions displace away from Nb^{5+} dominant cube faces. Thus, Pb ionic dis-

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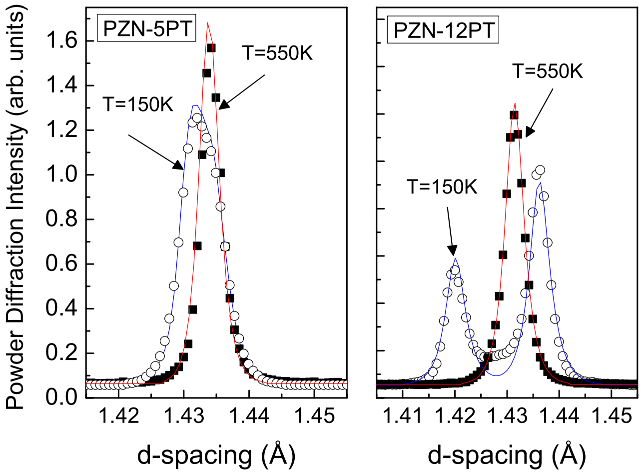

FIG. 1. (Color online) Selected powder-diffraction patterns (symbols) for PZN-5%PT and PZN-12%PT at 550 and 150 K. Solid lines represent fittings obtained from Rietveld refinements. The high-temperature [220] Bragg peak splits into a doublet due to the symmetry lowering at low temperature for both compounds.

placement varies depending on its nearest-neighbor B-site (Zn/Nb/Ti) configuration,[31] causing large structural disorder. In Rietveld refinement, static disorders tend to couple with thermal vibrations, rendering enlarged thermal parameters, which makes it difficult to study local Pb displacement and their medium-range correlation.

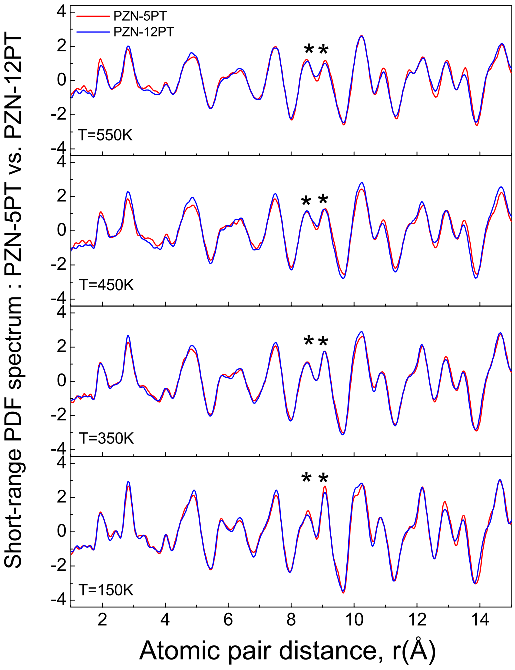

FIG. 2. (Color online) Comparison of short-range PDF spectrum ($r \leq 15$ Å) between PZN-5%PT and PZN-12%PT at temperatures of 550, 450, 350, and 150 K. PDF spectra are in remarkable agreement with each other at all temperatures. The relative intensity of the peaks marked by asterisk (*) grows rapidly with decreasing temperature.

Here it is worthwhile to mention that a double structure of two distinct phases was reported in closely related single-crystal PZN (Ref. 32) and PMN-10%PT.[33] In a single-crystal PZN, for example, it was found using high-energy x ray that the bulk structure is nearly cubic in contrast to rhombohedral distortion of the outer layer. However, later measurements on a different single-crystal PZN by neutron diffraction found no evidence for the nondistorted cubic bulk phase.[34] Thus, the double structure of rhombohedral/cubic lattice in single-crystal PZN is still controversial.

Now we move to short-range ionic correlations. In Fig. 2 we compare PDF spectra between PZN-5%PT and PZN-12%PT up to the pair distance $r = 15$ Å at four temperatures: 550, 450, 350, and 150 K. Here we found that the spectrum of PZN-5%PT matches well with that of PZN-12%PT at all

TABLE I. Atomic parameters of PZN-5%PT and PZN-12%PT at 150 K obtained from Rietveld refinements.

		PZN-5%PT	PZN-12%PT
Space group		$R3m$	$P4mm$
Lattice parameters (Å)	a	4.05296(8)	4.0165(1)
	b	4.05296(8)	4.0165(1)
	c	4.05296(8)	4.1091(1)
Angle (deg)	$\alpha=\beta=\gamma$	89.861(1)	90
Atomic positions (x,y,z)	Pb	$-0.0019(3), -0.0019(3), -0.0019(3)$	0.0, 0.0, 0.0
	Zn/Nb/Ti	0.4698(3), 0.4698(3), 0.4698(3)	0.5, 0.5, 0.4562(6)
	O1	0.4380(3), 0.4380(3), 0.4380(3)	$0.5, 0.5, -0.0838(9)$
	O2		0.5, 0.0, 0.3998(7)
Thermal parameters U_{iso} (Å^2)	Pb	0.0466(6)	0.0441(6)
	Zn/Nb/Ti	0.0049(2)	0.0038(3)
	O1	0.0196(2)	0.0193(5)
	O2		0.0152(3)
R-weighted pattern (Rwp) (%)		4.88	5.67
R-pattern (Rp) (%)		3.51	3.36

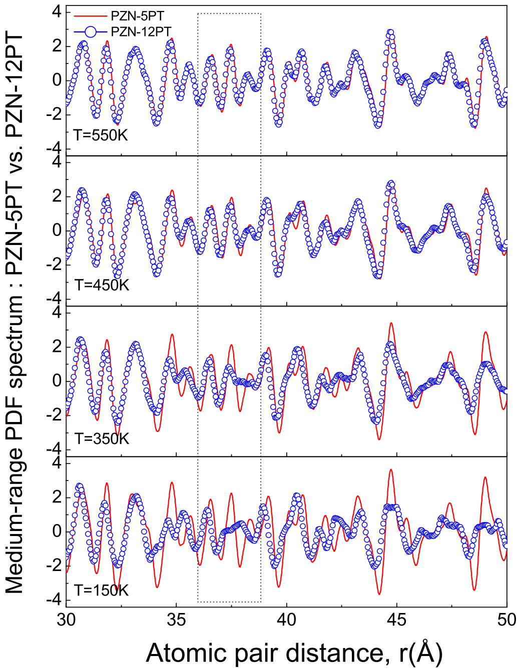

FIG. 3. (Color online) Temperature evolution of PDF spectrum in the r range $30 < r < 50$ Å for PZN-5%PT and PZN-12%PT. As the temperature decreases, the PDF peaks of PZN-5%PT get sharper without any noticeable change. By contrast, the PDF peaks split and redistribute in PZN-12%PT.

temperatures despite of their distinct low-temperature crystal structures. This is a remarkable result indicating that local ionic displacements do not change at cubic-rhombohedral and cubic-tetragonal phase transitions.[35] In addition, we note that the relative intensity of the peaks marked by asterisk (*) grows rapidly with decreasing temperature. Similar behavior was also observed in the prototypical relaxor ferroelectrics PMN and PZN and was ascribed to an increase in the volume fraction of PNRs with decreasing temperature.[10] Therefore, we conclude that ionic correlations on length scale $\xi \sim 15$ Å grow with decreasing temperature, independent of long-range crystal structure of PZN-5%PT and PZN-12%PT.

We further illuminate the evolution of a medium-range ($30 \leq r \leq 50$ Å) ionic ordering as a function of temperature. In Fig. 3, we find that the medium-range PDF spectra of the two compositions exhibit distinct temperature evolution. For PZN-5%PT, PDF peaks get sharper with decreasing temperature without any noticeable change in peak shape. In contrast, PDF peaks in PZN-12%PT split and intensities redistribute at and below $T \sim 450$ K. Overall, we find that the medium-range ionic pair correlations of PZN-5%PT and PZN-12%PT become distinct with decreasing temperature even though their short-range ionic correlations remain identical.

These temperature evolutions of PDF spectrum resemble to the order-disorder structural transitions observed in $BaTiO_3$ as a function of temperature. In $BaTiO_3$, Ti ions displace along eight equivalent ⟨111⟩ directions above Curie temperature. As the temperature decreases, however, antiferroelectric[36,37] coupling of local polarizations develops in one, two, and three dimensions to produce average orthorhombic, tetragonal, and cubic symmetries, respectively. Therefore, local structure of $BaTiO_3$ remains identical at all temperatures.[38] Only medium-range ionic pair correlations evolve as a result of the ordering of local Ti displacements and entailed structural transition. Likewise, we suggest that an order–disorder-type ordering of PNRs develops in PZN-5%PT and PZN-12%PT as a function of temperature and $PbTiO_3$ concentration. At high temperatures, small PNRs fluctuate between equivalent polar directions with average cubic symmetry. As the temperature decreases small PNRs align to form larger PNRs and gradually freeze with average rhombohedral symmetry in PZN-5%PT. In contrast, PNRs in PZN-12%PT do not align[39] as the local symmetry is different from the long-range crystal symmetry. Instead, equivalent PNRs undergo order–disorder-type ordering to induce average tetragonal symmetry with decreasing temperature similar to the case of PMN-28%PT under external electric field.[20] This scenario is supported by the suppression[40] of the diffuse scattering intensity in single-crystal PMN due to an ordering of PNRs under an external electric field below T_c as well as consistent with what we observed in the PDF spectrum of PZN-5%PT and PZN-12%PT as a function of temperature.

In conclusion, we found using temperature-dependent PDF analysis that relaxor ferroelectric PZN-5%PT and PZN-12%PT have almost identical atomic-pair correlations up to $r \sim 15$ Å from 550 to 150 K despite their differences in low-temperature crystal symmetry. In the farther atomic range $30 < r < 50$ Å, however, they start to diverge from each other below $T \sim 450$ K. These PDF results suggest that an order–disorder-type ordering of PNRs develops with decreasing temperature, which is quite similar to the order-disorder behavior of local Ti displacements in $BaTiO_3$. The order-disorder behavior of PNRs imposes an important consequence on the mechanism of polarization rotation which is believed to play a major role in the giant electromechanical coupling in relaxor ferroelectrics and thus requires further experimental and theoretical studies.

This work was supported by the Korea Research Foundation Grant funded by the Korean Government (Grants No. KRF-2007-331-C00087 and No. KRF-2006-005-J02804). I.-K.J. thanks J. K. Lee for providing samples used in this study. Neutron diffraction measurements have benefited from the use of NPDF at the Lujan Center at Los Alamos Neutron Science Center funded by DOE Office of Basic Energy Sciences. Los Alamos National Laboratory is operated by Los Alamos National Security LLC under DOE Contract No. DE-AC52-06NA25396. The upgrade of NPDF was funded by NSF through Grant No. DMR 00-76488.

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*Author to whom correspondence should be addressed; jeong@pusan.ac.kr

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