Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Origin of polar nanoregions from displacive-correlation in relaxor ferroelectric $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$

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Supplemental Materials

Figure S1. Rietveld refinement results of bank 4 data from the time-of-flight neutron scattering experiments at (a) 50 K, (b) 120 K, and (c) 200 K. The diffraction data at low temperatures do not show obvious changes in peak shapes and intensities, which indicates that there is no structural phase transition over the range of 50 K < T < 200 K. The gray circles represent the experiment data, the orange solid lines are the calculated data obtained from GSAS, and the light green lines give the difference between experimental and calculated data.

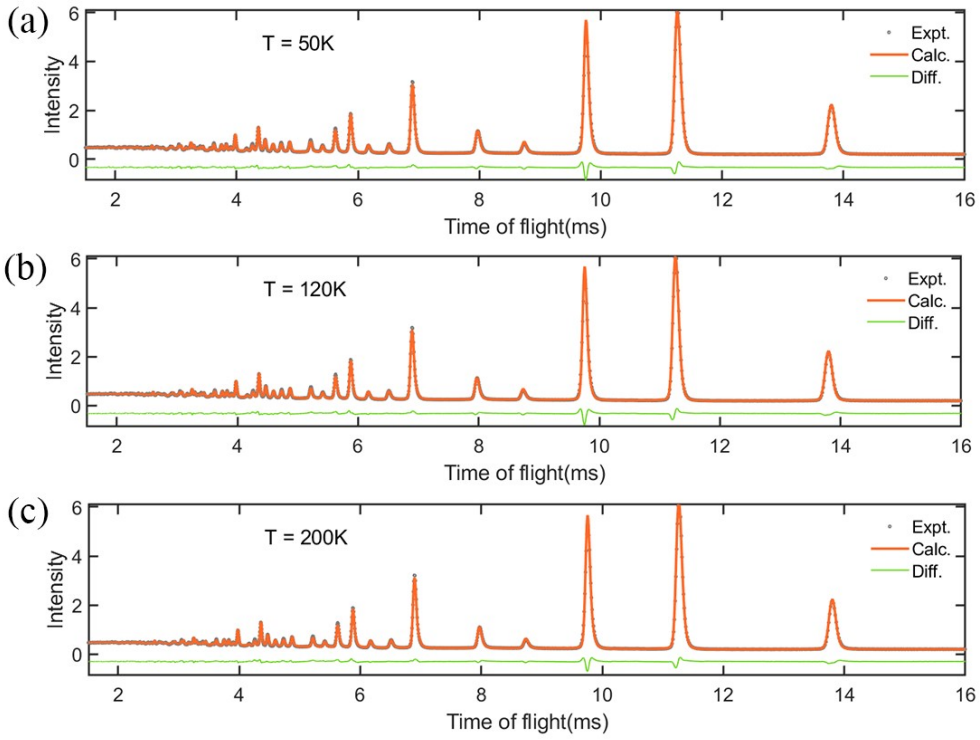

Figure S2. Comparison of the PDF data in different ranges at 50 K, 120 K, and 200 K: (a) the range of 0-15 Å; (b) the range of 15-30 Å; and (c) the range of 30-45 Å. The variation mainly manifests in the range of 0-15 Å, and barely noticeable changes occur in the range of 15-45 Å.

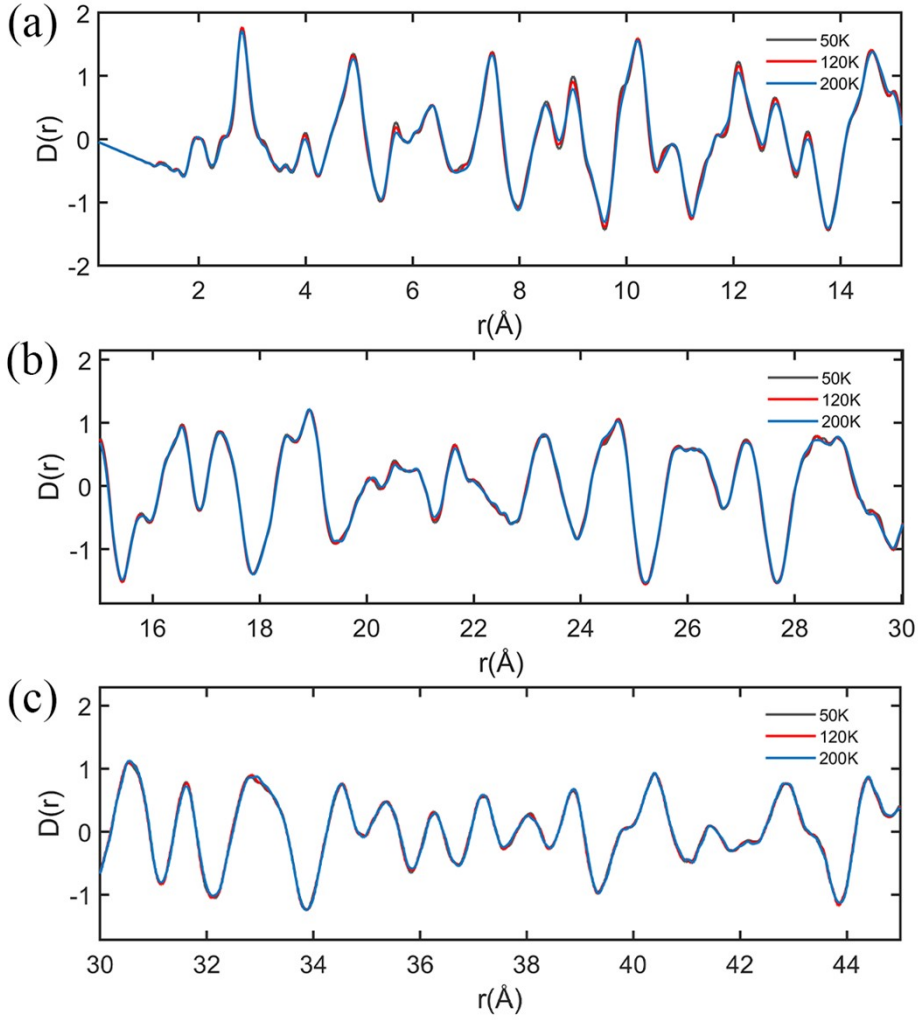

Figure S3. PDFFit result for PMN-28PT in the range of 1.5-45 Å fitted by the *M* model. The black circles represent the experimental data, the solid orange lines show the simulated data, and the light green lines indicate the difference between the experimental and calculated data.

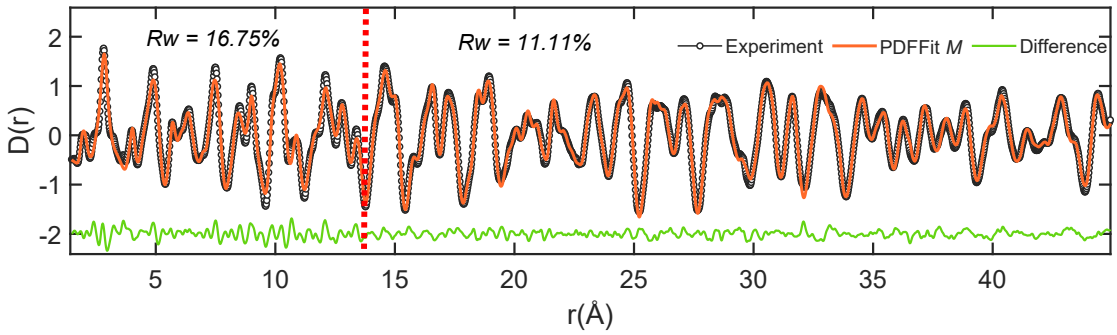

Figure S4. Stereographic-projection maps of the Pb-displacement in the ordered region (a) and the disordered regions (b) at 50K. Either in the ordered regions or in the disordered regions, the Pb atoms displace mainly in the monoclinic mirror planes with a small deviation from the <111>$_{pc}$ direction. (c) A stereographic schematic for an ideal cubic crystal viewed along the <111>$_{pc}$ direction. The major pseudocubic directions, namely, tetragonal (*T*), rhombohedral (*R*), and orthorhombic (*O*), are marked.

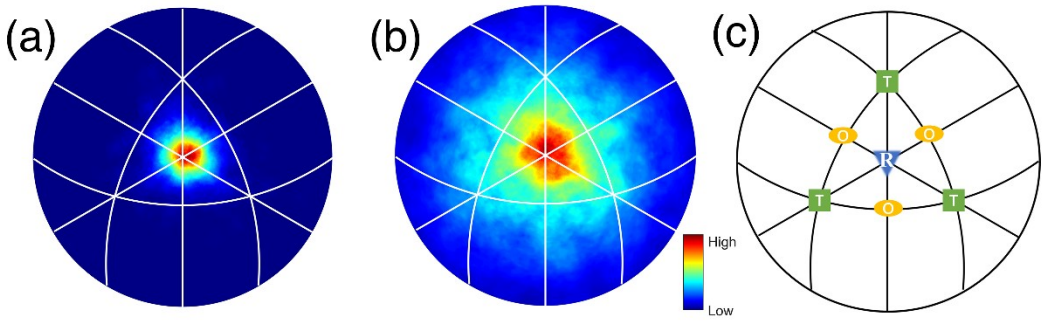

Figure S5. Stereographic-projection maps viewed down <111>$_{pc}$ for the displacement of Ti, Nb, and Mg ions at 50 K.

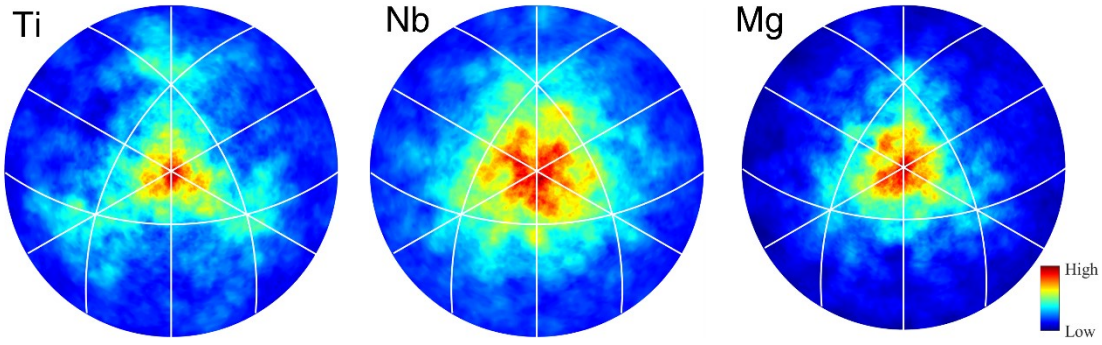

Figure S6. The fitting result of PDF and *F*(*Q*) in RMC modeling at three studied temperatures. (a) PDF fitting at 50 K; (b) *F*(*Q*) fitting at 50 K; (c) PDF fitting at 120 K; (d) *F*(*Q*) fitting at 120 K; (e) PDF fitting at 200 K; and (f) *F*(*Q*) fitting at 200 K. The insets in (b), (d), and (f) are the enlarged high-*Q* sections (28-40 Å) of (b), (d), and (f), respectively.

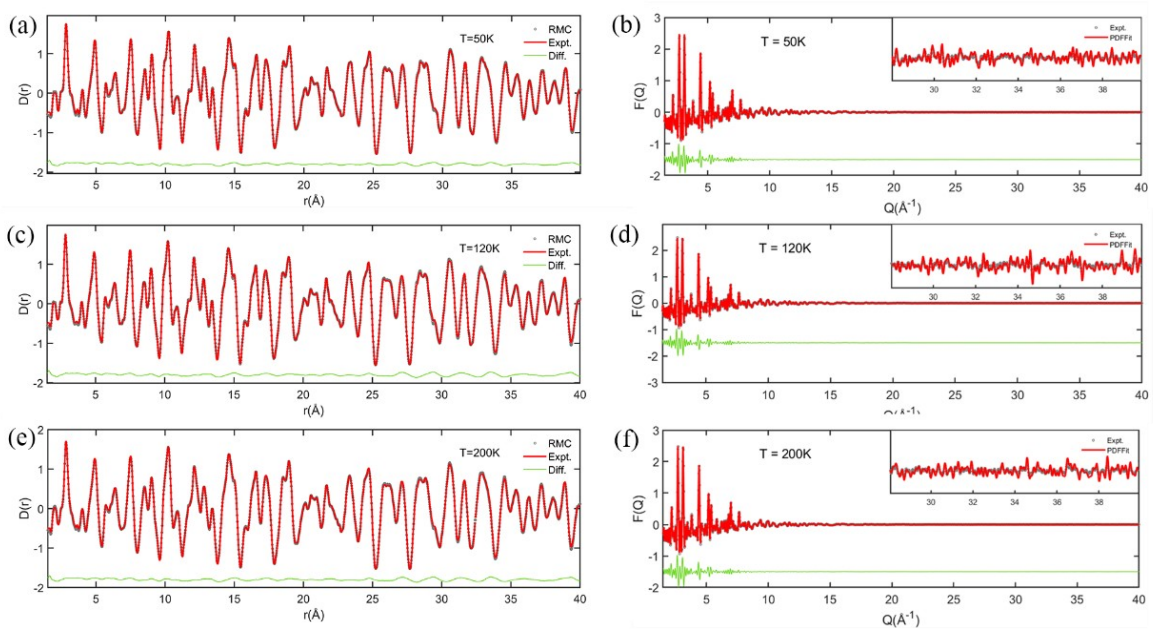

Figure S7. RMC refinement results on different stages during the refining process at 120 K and 200 K. (a) the stereographic projections viewed down <001>$_{pc}$ for Pb atomic displacements; (b) the comparison between experimental PDF and refined PDF; (c) the three-dimensional Pb-displacement correlation distribution, where the red regions are the clusters Pb atoms with correlation coefficients c_{ij} above 0.9. The RMC refinement process for 50 K is similar to 120 K and 200 K.

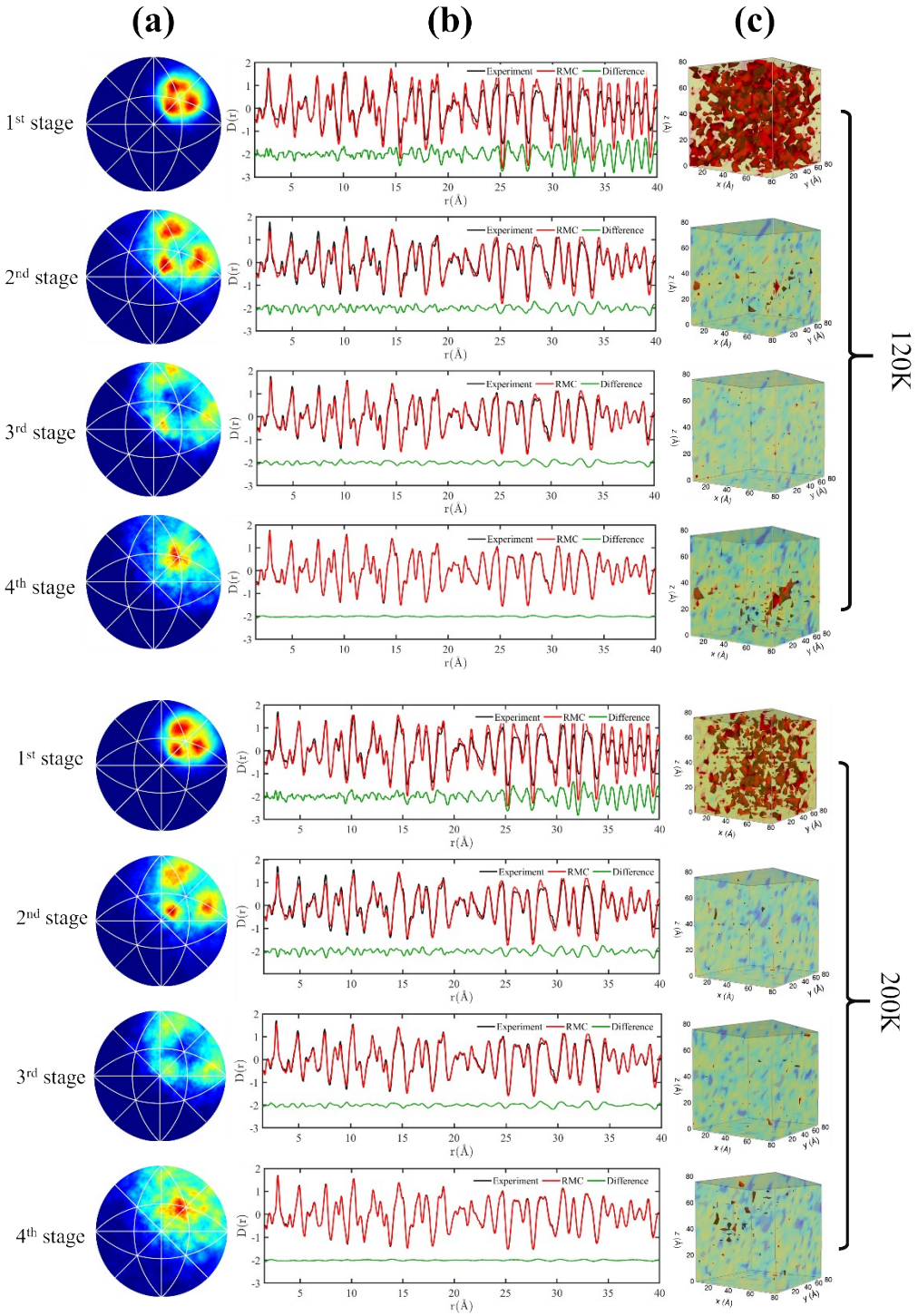

Table S1. Rietveld refinement parameters for PMN-28PT at low temperatures. The free structural parameters are presented by Pb (½+*s*, ½+*s*, ½+*s*), Mg/Nb/Ti (*t*, *t*, *t*), and O (*d*, ½-2*d*, *d*) [1]. The parameters *s* and *t* represent the displacements of the Pb atom and *B*-site atom along the polar axis [111] $_{pc}$ and *d* is the octahedral distortion.

Temperature	50 K	120 K	200 K
a (Å)	4.02250(6)	4.02235(6)	4.02274(5)
α (°)	89.800(1)	89.8139(9)	89.8344(9)
s (Å)	0.0433(1)	0.0419(1)	0.0419 (1)
t (Å)	0.0120 (2)	0.0118 (2)	0.0135(3)
d (Å)	-0.0105(1)	-0.0103(1)	-0.0076(1)
U_{iso}_Pb (Å^2)	0.0215(3)	0.0233(3)	0.0257(3)
U_{iso}_Mg/Nb/Ti (Å^2)	0.0017(2)	0.0019(2)	0.0022(1)
U_{iso}_O (Å^2)	0.0102(1)	0.0108(1)	0.0118(1)
R_{wp}	0.047	0.043	0.039

[1] H. D.Megaw and C.N.W.Darlington, Acta Crystallogr. Sect. A **31**, 161 (1975).

Table S2. Structural parameters obtained from PDFFit at 50 K for the fitting of the PDF data in the range of 1.5–40 Å using the rhombohedral structure with isotropic thermal displacement parameters.

Lattice parameters	***a* (Å)**	**4.024 (1) Å**
	α (°)	**89.65(5)°**
Structural parameters (Å)	***s***	0.056(3)
	t_Mg	0.025(8)
	t_Nb	0.022(3)
	t_Ti	0.020(10)
	d	-0.004(1)
Thermal parameters U_{iso} (Å²)	U_{iso}**_Pb**	0.029(4)
	U_{iso}**_Mg**	0.005(7)
	U_{iso}**_Nb**	0.005(2)
	U_{iso}**_Ti**	0.008(13)
	U_{iso}**_O**	0.014(1)
***Rw* (%)**		15.9

Table S3. Short-range (0-15 Å) structural parameters obtained from PDFFit refinements for PMN-28PT with *R* model and *M* model at 50 K.

***R* model**	**a = b = c = 4.020(4) Å, α = β = γ = 89.7(1) °**				
	Atoms	***x***	***y***	***z***	U_{iso}
	Pb	0.557(3)	0.557	0.557	0.016(3)
	Mg	0.027(8)	0.027	0.027	0.001(5)
	Nb	0.019(5)	0.019	0.019	0.008(4)
	Ti	0.02(1)	0.02	0.02	0.01(2)
	O	0.506(4)	-0.003(2)	-0.003(2)	0.010(1)
***M* model**	**a =5.72(1) Å, b = 5.66(1) Å, c = 4.00(1) Å, α = γ = 90.0°, β = 89.8(4) °**				
	Atoms	***x***	***y***	***z***	U_{iso}
	Pb	0.053(5)	0.0	0.04(1)	0.019(5)
	Mg	0.52(1)	0.0	0.48(4)	0.001 (6)
	Nb	0.525(4)	0.0	0.483(1)	0.001(2)
	Ti	0.52(2)	0.0	0.48(4)	0.001(4)
	O1	0.500(9)	0.0	-0.01(2)	0.007 (1)
	O2	0.244(5)	0.240(4)	0.49(1)	0.010(1)

Table S4. Structural parameters obtained from PDFFit refinements using the *R* model and the *M* model over the ranges of 15-30 Å and 30-45 Å at 50 K.

	a = b = c = 4.024(2) Å, α = β = γ = 89.6(1) °				
	Atoms	***x***	***y***	***z***	U_{iso}
***R* model**	**Pb**	0.552(5)	0.552	0.552	0.030(6)
	Mg	0.02(1)	0.02	0.02	0.002(8)
(15-30Å)	**Nb**	0.018(7)	0.018	0.018	0.009(6)
	Ti	0.02(1)	0.02	0.02	0.003(13)
	O	0.511(4)	-0.005(2)	-0.005	0.014(2)
	a =5.729(9) Å, b = 5.682(7) Å, c = 4.007(5) Å, α = γ = 90.0°, β = 89.6(3) °				
	Atoms	***x***	***y***	***z***	U_{iso}
***M* model**	**Pb**	0.056(8)	0.0	0.01(2)	0.035(7)
	Mg	0.55(2)	0.0	0.51(6)	0.002 (11)
(15-30Å)	**Nb**	0.50 (1)	0.0	0.50(1)	0.003(4)
	Ti	0.52(2)	0.0	0.49(4)	0.002(15)
	O1	0.51(1)	0.0	0.002(21)	0.011(1)
	O2	0.247(7)	0.232(5)	0.47(1)	0.011(2)

	a = b = c = 4.023(1) Å, α = β = γ = 89.7(1) °				
	Atoms	***x***	***y***	***z***	U_{iso}
***R* model**	**Pb**	0.549(8)	0.549	0.549	0.036(8)
	Mg	0.02(2)	0.02	0.02	0.002(9)
(30-45Å)	**Nb**	0.01(1)	0.01	0.01	0.011(12)
	Ti	0.02(3)	0.02	0.02	0.003(20)
	O	0.509(6)	-0.004(3)	-0.004	0.023(3)
	a =5.733(7) Å, b = 5.675(5) Å , c = 4.009(3) Å, α = γ = 90.0°, β = 89.8(3) °				
	Atoms	***x***	***y***	***z***	U_{iso}
***M* model**	**Pb**	0.05(1)	0.0	0.03(2)	0.032(8)
	Mg	0.56(3)	0.0	0.48(7)	0.002(20)
(30-45Å)	**Nb**	0.511(9)	0.0	0.48(1)	0.002(6)
	Ti	0.51(3)	0.0	0.49(4)	0.001(6)
	O1	0.49(2)	0.0	-0.02(2)	0.007 (1)
	O2	0.252(9)	0.237(6)	0.51(2)	0.017(3)