crystals

Origin of Structural Change Driven by A-Site Lanthanide Doping in ABO_3-Type Perovskite Ferroelectrics

Lan Xu [1,2], Zujian Wang [1,2], Bin Su [1,3], Chenxi Wang [1], Xiaoming Yang [1], Rongbing Su [1], Xifa Long [1,2,3] and Chao He [1,2,3,*]

[1] Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, 350002, China; xulan@fjirsm.ac.cn (L.X.); wangzujian@fjirsm.ac.cn (Z.W.); subin@fjirsm.ac.cn (B.S.); cxwong123@outlook.com (C.W.); xmyang@fjirsm.ac.cn (X.Y.); surongbing@fjirsm.ac.cn (R.S.); lxf@fjirsm.ac.cn (X.L.)

[2] Fujian Science & Technology Innovation Laboratory for Optoelectronic Information of China, Fuzhou, 350108, China

[3] Fujian College, University of Chinese Academy of Sciences, Fuzhou, 350002, China

* Correspondence: hechao@fjirsm.ac.cn

Supplement materials

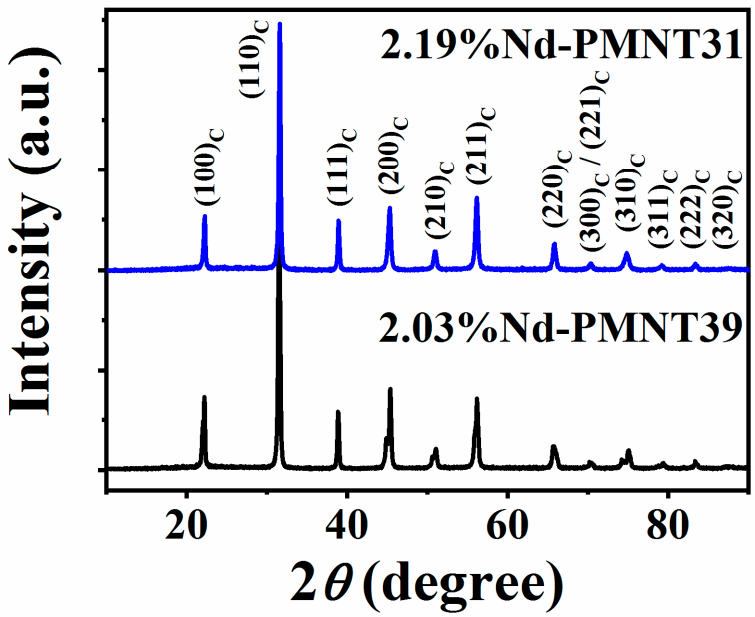

Figure S1. XRD patterns of 2.19%Nd-PMNT31 and 2.03%Nd-PMNT39 crystals, indexed to $Pm\bar{3}m$ cubic system.

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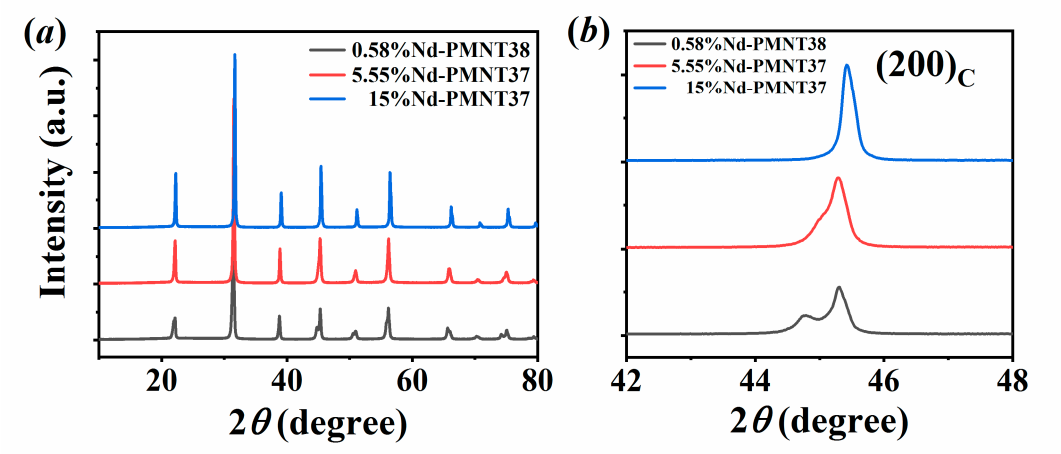

Figure S2. (a) The powder XRD patterns of Nd-PMNT crystals and (b) the enlarged (200)c reflections of the different compositions.

Table S1. Lattice parameters, cell volumes and theoretical densities of Nd-PMNT crystals based on the Rietveld refinement.

Samples	Space group (fractions)	a and b (Å)	c (Å)	$\alpha = \beta = \gamma$	Cell volume (Å^3)	ρ (g/cm^3)
0.58%Nd-PMNT38	$P4mm$ (100 wt%)	4.0017	4.0423	90^o	64.73	7.874
5.55%Nd-PMNT37	$P4mm$ (71 wt%)	4.0143	4.0356	90^o	65.03	7.896
	$Pm\bar{3}m$ (29 wt%)	3.9089	3.9089	90^o	59.73	8.874
15%Nd-PMNT37	$Pm\bar{3}m$ (100 wt%)	3.9888	3.9888	90^o	63.46	8.392

Table S2. Fractional coordinates (*x*, *y* and *z*) and U_{iso} of all atoms of Nd-PMNT crystals for Rietveld refinement.

Samples	Space Group (Fractions)	Atom (Wyckoff site, Symmetry)	(*x*, *y*, *z*) and U_{iso}
0.58%Nd-PMNT38	*P*4*mm* (100 wt%)	Pb/Nd (1*a*, 4*mm*)	(0, 0, 0), 0.02784
		Mg/Nb/Ti (1*b*, 4*mm*)	(0.5, 0.5, 0.54112), 0.00239
		O1 (1*b*, 4*mm*)	(0.5, 0.5, 0.07096), 0.01582
		O2 (2*c*, 2*mm*)	(0.5, 0, 0.58177), 0.00367
5.55%Nd-PMNT37	*P*4*mm* (71 wt%)	Pb/Nd (1*a*, 4*mm*)	(0, 0, 0), 0.03647
		Mg/Nb/Ti (1*b*, 4*mm*)	(0.5, 0.5, 0.53236), 0.0112
		O1 (1*b*, 4*mm*)	(0.5, 0.5, 0.0806), 0.00822
		O2 (2*c*, 2*mm*)	(0.5, 0.0, 0.54557), 0.03534
	$Pm\bar{3}m$ (29 wt%)	Pb/Nd (1*a*, $m\bar{3}m$)	(0, 0, 0), 0.03862
		Mg/Nb/Ti (1*b*, $m\bar{3}m$)	(0.5, 0.5, 0.5), 0.01236
		O (3*c*, 4/*mm.m*)	(0.5, 0.5, 0), 0.02844
15%Nd-PMNT37	$Pm\bar{3}m$ (100 wt%)	Pb/Nd (1*a*, $m\bar{3}m$)	(0, 0, 0), 03931
		Mg/Nb/Ti (1*b*, $m\bar{3}m$)	(0.5, 0.5, 0.5), 0.01037
		O (3*c*, 4/*mm.m*)	(0.5, 0.5, 0), 0.03259

Table S3. The Shannon ionic radii [22], bond strengths in diatomic molecules at 298 K [56] of Pb^{2+}, Ba^{2+}, Ti^{4+}, Mg^{2+}, Nb^{5+} and lanthanide ions commonly used in perovskite ferroelectric materials.

Ions	Ion radius in 12-coordinate (Å)	Ion radius in 6-coordinate (Å)	Molecule	Bond strengths (kJ/mol)
La^{3+}	1.36	1.032	La-O	799
Ce^{3+}	1.34	1.01	Ce-O	795
Pr^{3+}	-	0.99	Pr-O	753
Nd^{3+}	1.27	0.983	Nd-O	703
Pm^{3+}	-	0.97	Pm-O	674
Sm^{3+}	1.24	0.958	Sm-O	565
Eu^{3+}	-	0.947	Eu-O	479
Gd^{3+}	-	0.938	Gd-O	719
Tb^{3+}	-	0.923	Tb-O	711
Dy^{3+}	-	0.912	Dy-O	607
Ho^{3+}	-	0.901	Ho-O	611
Er^{3+}	-	0.89	Er-O	615
Tm^{3+}	-	0.88	Tm-O	502
Yb^{3+}	-	0.868	Yb-O	397
Lu^{3+}	-	0.861	Lu-O	678
Ce^{4+}	1.14	0.87	-	-
Pr^{4+}	-	0.85	-	-
Pb^{2+}	1.49	-	Pb-O	382
Ba^{2+}	1.61	-	Ba-O	561.9
Ti^{4+}	-	0.605	Ti-O	672.4
Mg^{2+}	-	0.72	Mg-O	363.2
Nb^{5+}	-	0.64	Nb-O	771.5

Table S4. The previous reported ions occupancy of lanthanide ions in $PbTiO_3$ and $BaTiO_3$.

	$PbTiO_3$			$BaTiO_3$		
	A-site	B-site	A-site+ B-site	A-site	B-site	A-site + B-site
La	√	-	-	√	-	-
Ce	-	-	-	√	√	-
Pr	√	-	-	-	-	-
Nd	√	-	-	√	-	-
Pm	-	-	-	-	-	-
Sm	√	-	-	√	-	-
Eu	√	-	-	√	√	√
Gd	-	-	√	√	√	√
Tb	-	-	-	√	√	√
Dy	-	-	√	√	√	√
Ho	-	-	-	√	√	√
Er	√	-	-	√	√	√
Tm	-	-	-	-	-	-
Yb	-	-	-	√	√	-
Lu	-	-	-	-	-	-

Table S5. The decrease rate of T_C in $PbTiO_3$ and $BaTiO_3$ systems with increasing A-site Ln doping contents (≥ 5 at%).

Sample	Decrease rate of T_C	Ref.	Sample	Decrease rate of T_C	Ref.
La-$PbTiO_3$	~20.87 K/at%	[24]	La-$BaTiO_3$	~19.45 K/at%	[53]
Pr-$PbTiO_3$	~13.87 K/at%	[25]	-	-	-
Nd-$PbTiO_3$	~18.5 K/at%	[26]	Nd-$BaTiO_3$	~18.95 K/at%	[29]
Sm-$PbTiO_3$	~16.7 K/at%	[27]	Sm-$BaTiO_3$	~6.93 K/at%	[31]