PHYSICAL REVIEW B, VOLUME 65, 064106

Monoclinic structure of unpoled morphotropic high piezoelectric PMN-PT and PZN-PT compounds

Jean-Michel Kiat,[1,2] Yoshiaki Uesu,[3] Brahim Dkhil,[1] Masaaki Matsuda,[4] Charlotte Malibert,[1,5] and Gilbert Calvarin[1]
[1]*Laboratoire Structures, Propriétés et Modélisation des Solides, Ecole Centrale, Grande Voie des Vignes, 92295 Châtenay-Malabry Cedex, France*
[2]*Laboratoire Léon Brillouin, CE Saclay, 91191 Gif-sur-Yvette Cedex, France*
[3]*Department of Physics, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan*
[4]*Advanced Science Research Center, Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-1195, Japan*
[5]*Laboratoire des Multicouches Nanométriques, Université d'Evry Val d'Essonne, 91000 Evry, France*

(Received 26 September 2001; published 17 January 2002)

Evidences of a monoclinic phase in unpoled $(\mathrm{PbMg_{1/3}Nb_{2/3}O_3})_{1-x}$-$(\mathrm{PbTiO_3})_x$ with $x=0.35$ (PMN-PT 35%) and unpoled $(\mathrm{PbZn_{1/3}Nb_{2/3}O_3})_{1-x}$-$(\mathrm{PbTiO_3})_x$ with $x=0.09$ (PZN-PT 9%) are presented from a neutron Rietveld analysis. This monoclinic phase is different from the phase recently evidenced by Noheda and co-workers in $\mathrm{PbZr_{1-x}Ti_xO_3}$ with $x=0.48$ [B. Noheda *et al.*, Phys. Rev. B. **61**, 8687 (2000)] but is identical to the phase observed in poled PZN-PT with $x=0.08$ [B. Noheda *et al.*, Phys. Rev. Lett. **86**, 3891 (2001)] by the same authors. The structural resolutions allowed us to compare both structures and to deduce the direction and magnitude of polarization. In PMN-PT 35% and PZN-PT 9% this phase is characterized by a weak value of polarization, a strong deformation of oxygen polyhedra, and weak cationic shifts.

DOI: 10.1103/PhysRevB.65.064106 PACS number(s): 61.50.−f, 77.80.−e

The study of the ultrahigh piezoelectricic, dielectric, and electromechanical responses in perovskites lead-based oxides is a challenging area in which both experimental and theoretical works are of equal importance to obtain a comprehensive explanation. These high responses are observed in regions of phase diagrams such as $\mathrm{PbZr_{1-x}Ti_xO_3}$ [piezoelectric transducer (PZT), with $x\approx0.48$], $(\mathrm{PbZn_{1/3}Nb_{2/3}O_3})_{1-x}$-$(\mathrm{PbTiO_3})_x$ (PZN-PT, with $x\approx0.08$), $(\mathrm{PbMg_{1/3}Nb_{2/3}O_3})_{1-x}$-$(\mathrm{PbTiO_3})_x$ (PMN-PT, with $x\approx0.35$), $(\mathrm{PbSc_{1/2}Nb_{1/2}O_3})_{1-x}$-$(\mathrm{PbTiO_3})_x$ (PSN-PT with $x\approx0.43$) etc., called morphotropic phase boundaries, which separate two ferroelectric phases with different orientations of the polarization. Up to now the structure of these morphotropic compounds was thought to be a mixing of the two adjacent ferroelectric phases and the local texture that results from these competing phases was supposed to explain the high responses of these materials.

However very recently, experimental and theoretical breakthroughs have been achieved. Indeed the observation of two new monoclinic phases in the concentration-temperature-electric-field phase diagrams of PZT (Ref. 1) and PZN-PT (Ref. 2) morphotropic compounds that should connect both adjacent ferro phases provided a new perspective for understanding the outstanding properties of these materials. These new phases display different orientations of the polarization (Fig. 1), inside the (110) plane for PZT 48% (space group *Cm* with monoclinic *b* axis along [110] direction) and inside the (010) plane for PZN-PT 9% (space group *Pm* with monoclinic *b* axis along [010] direction) whereas the polarization stands along [111] and [001] directions in the adjacent rhombohedral and tetragonal phases, respectively. In the case of poled PZN-PT a synchrotron study showed that this monoclinic phase could have *a*- and *c*-lattice parameters with same value and degenerate, therefore, into a *B*-centered orthorhombic phase.[3]

In fact these new phases allow the two possible paths of polarization rotation between the tetragonal phase (high-titanium-concentration region) and the rhombohedral phase (low-titanium-concentration region), in accordance with theoretical considerations by Fu and Cohen[4] and by Vanderbilt and Cohen.[5]

The purpose of this paper is to report a neutron Rietveld analysis of unpoled PMN-PT ($x=0.35$) and unpoled PZN-PT ($x=0.09$) compounds, which has allowed us to evidence the existence of such a new phase in both compounds. This monoclinic phase is different from the phase recently evidenced by Noheda and co-workers in $\mathrm{PbZr_{1-x}Ti_xO_3}$ with $x=0.48$ (Ref. 1) but is identical to the phase observed in poled PZN-PT with $x=0.08$ (Ref. 2) by the same authors. These structural resolutions allowed us to compare both structures and to deduce the direction and magnitude of polarization in both compounds.

Well-crystallized powdered samples of PMN-PT 35% were prepared using the classical method by Swartz and Shrout[6] in which the columbite precursor is first synthesized to avoid formation of parasitic pyrochlore phases. A powdered sample of PZN-PT 9% has been obtained by grinding a single-crystal growth by the flux method and kindly provided by Yamashita from Toshiba company. The different samples were annealed at 800 °C during 1 h to avoid possible residual strains.

The neutron experiments were performed at Laboratoire Léon Brillouin using the Orphée reactor facilities (Saclay, France) for PMN-PT 35% at 90 K and at $\lambda=1.226$ Å, and at JAERI (Japan) for PZN-PT 9% at 35 K and $\lambda=1.820$ Å, both on thermal sources. Powder diffraction patterns were collected on high resolution two-axis goniometers between 0 and 160 2Θ degrees. Structural refinements were carried out with the XND (Ref. 7) and FULLPROF (Ref. 8) programs.

In PZN-PT 9% strong splitting of *h*00, *hh*0, and *hhh* peaks were evidenced, whereas in PMN-PT 35% these dis-

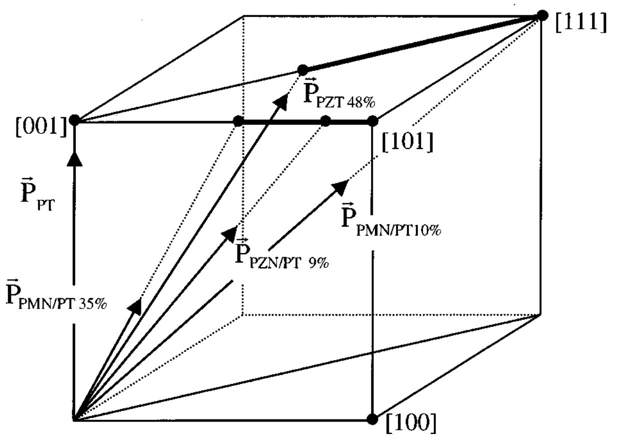

FIG. 1. Direction of the polarization in the tetragonal phase of PT, in the rhombohedral phase of PMN-PT 10% (from Ref. 10), in the Pm phase of PMN-PT 35% and PZN-PT 9% (this work) and in the Cm phase of PZT 48% (from Ref. 1).

tortions were only detected from widening in the profiles (Fig. 2). At this point there were two possible interpretations for these profiles: (1) a mixing of two phases, for instance, tetragonal and rhombohedral as naturally suggested by the adjacent phases of the morphotropic boundaries and (2) the existence of sole low-symmetry distortion of the cubic phase, as suggested by the new experimental and theoretical ideas mentioned above.

We have proceeded in several steps for the analysis of the patterns. At first, in order to test all possible combinations of phases, we have performed a profile-matching analysis of the full patterns using the FULLPROF program. The principle of this analysis is to fit (pseudovoigt profiles) the full pattern without any structural hypothesis, except those imposed by the symmetry of the space group. These results showed unambiguously a *Pm* phase in the case of PMN-PT 35%, whereas in the case of PZN-PT 9% only poor agreement was obtained with a single monoclinic phase that could be, at this stage of the refinement, *Pm* or *Cm* as well; in particular, we were able to exclude the existence of a *B*-centered ortho-

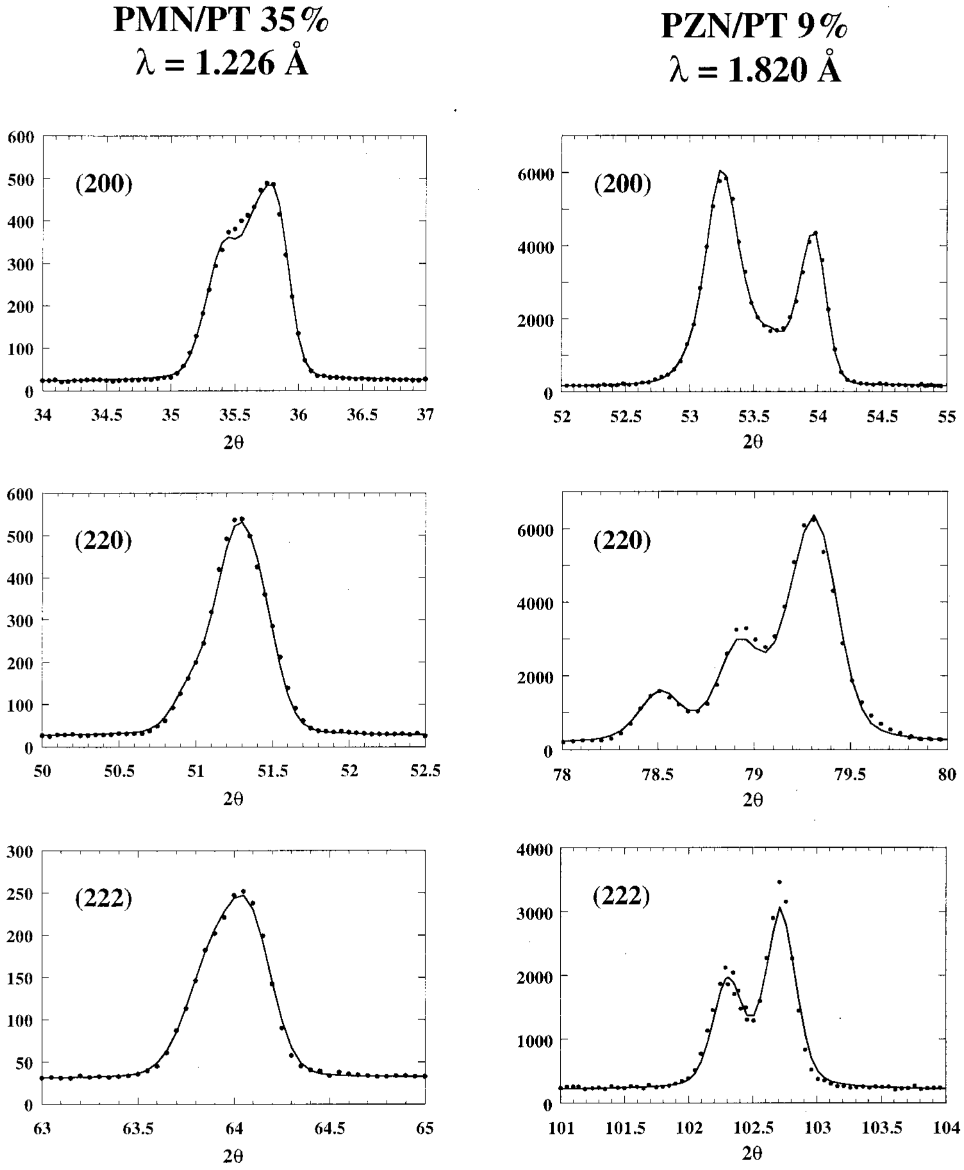

FIG. 2. Typical parts of the neutron pattern showing the splittings of the cubic Bragg peaks: experimental points and solid lines calculated from the Rietveld refinements.

rhombic distortion. For this last compound a further step was achieved by testing combination of different phases, monoclinic *Pm*, *Cm*, tetragonal $P4mm$, and rhombohedral $R3m$ etc. These results showed possible combinations of the *Pm* or *Cm* monoclinic phases with a minor existence (few percent) of a tetragonal $P4mm$ phase.

This preliminary study having restricted the possible structural models to be tested, we have afterward proceeded to the Rietveld analysis using the XND program. As pointed out by Noheda *et al.*[1] in their study of PZT 48%, a key point of the analysis of such compounds is the introduction of anisotropic peak broadening (i.e., profile with a *hkl* dependence). Indeed, for instance, in the case of PMN-PT 35% the monoclinic *Pm* model with conventional profiles gave 7.46%, 5.53%, and 1.87% values for Rwp, Rb, and G.o.F., respectively, whereas these values reduced to 5.40%, 3.76%, and 1.35% when anisotropic profiles were introduced. This anisotropy is most probably related to the anisotropic shape of the ferroelectric domains as evidenced in PZN-PT 9% by optical observations.[9] However it is important to notice that for both compounds the structural solutions were the same using isotropic or anisotropic profiles. At the end of the refinements isotropic *B* thermal parameters were released towards anisotropic factors but only small improvements were obtained.

In the case of PZN-PT 9% the Rietveld analysis allowed to exclude the $Cm+P4mm$ model that gave poorer agreement factors (10.85%, 5.11%, and 1.96%) than the $Pm+P4mm$ model (7.99%, 3.83%, and 1.44%); but although the two phases $Pm+P4mm$ model gave better agreement than a sole *Pm* phase, the refinement showed only about 1% of the sample was in the $P4mm$ tetragonal phase, as deduced from the scale factors ratio of the fitting.

In Table I, we have summarized the results of the structural monoclinic model for both compounds. Additional proof of the existence of a ‘‘true’’ monoclinic phase is the observation of O2 and O3 independent atomic positions, i.e., not deduced by a *B* (1/2 0 1/2) translation as it should be in the case of a *B* orthorhombic phase. Classically, strong thermal parameters are observed for the lead atoms in both compounds, as also observed in the study of PMN (Ref. 10) PZT (Ref. 1) and our study of relaxor PMN-PT 10% (Ref. 11) and PSN (Ref. 12) for instance. But contrarily to what is observed in these compounds, we could not reduce these high values by introducing disordered shifts from the special positions: moreover, we could not conclude about a possible direction of disorder when changing isotropic thermal parameters into anisotropic parameters. We believe, however, that these high-*B* values for the lead atoms arise most probably from the existence of disorder, like in other relaxors, which could not be evidenced here due to the important number of parameters (structural and profile) to be refined.

The results show that the oxygen polyhedra (cuboctahedra around the Pb cations and octahedra around the Mg/Nb/Zn/Ti cations) are strongly distorted: indeed O-O distances splits into values in between 2.70 Å and 3.00 Å in PMN-PT 35%, and between 2.61 Å and 3.15 Å in PZN-PT 9%, whereas these values are closer in other ferroelectric compounds: between 2.81 Å and 2.95 Å in PSN (Ref. 12), 2.80 Å and 2.91 Å in PMN-PT 10% (Ref. 11), in PZT (Ref. 1) the distortion of the oxygen polyhedra is intermediate: O-O distances are in between 2.78 and 2.98 Å.

TABLE I. Structural results for the Pm phase of PMN-PT 35% and PZN-PT 9%.

	PMN-PT 35%	PZN-PT 9%
a, b, c (Å)	4.0344, 3.9873, 4.0092	4.0608, 4.0084, 4.0529
β (°)	90.26	90.25
Pb		
x, y, z	0, 0, 0	0, 0, 0
Beq Å^2	2.40	2.80
Ti/Mg/Zn/Nb		
x, y, z	0.5407, 0.5, 0.4841	0.5289, 0.5, 0.4748
Beq Å^2	0.39	0.63
O1		
x, y, z	0.5889, 0, 0.4520	0.5882, 0, 0.4561
Beq Å^2	0.24	0.26
O2		
x, y, z	0.0052, 0.5, 0.5012	−0.0060, 0.5, 0.5285
Beq Å^2	0.68	1.03
O3		
x, y, z	0.5102, 0.5, 0.0046	0.5235, 0.5, 0.0090
Beq Å^2	0.62	0.17
Rwp	5.40	7.99
Rb	3.76	3.83
G.o.F.	1.35	1.44

Compared with the cubic paraelectric phase, the cubic 12-fold degenerated Pb-O distance inside the oxygen cuboctahedron splits into eight types of directions, one of which being very short (2.46 Å for PMN-PT 35% and 2.50 Å for PZN-05 9%), and another one being very large (3.24 Å and 3.26 Å). The cubic sixfold degenerated Mg/Nb/Zn/Ti-O distance inside the oxygen octahedron splits into five distances that are in between 1.87 and 2.16 Å and 1.89 and 2.18 Å, respectively. Consequently the *Pm* monoclinic structure is characterized by strong distortions of the oxygen polyhedra but with weak shifts of the lead atoms and of the Mg/Nb/Zn/Ti cations inside these polyhedra. Indeed, this is shown by the values of the δ ferro shifts (i.e., shifts of the cations from the barycenter of the O atoms), summarized in Table II in which we compare also with ferroelectric perovskite $BaTiO_3$ and $PbTiO_3$ (from the work by Hewat[13] and Nelmes *et al.*[14]) and with relaxor PSN (Ref. 12) PMN-PT 10% (Ref. 11) and PZT 48% (Ref. 1) (calculated from the published data); the closest cubic direction for each of these displacements is indicated. Comparison of these data reveals almost identical δ shifts in both PMN-PT 35% and PZN-PT 9% that are weak for the lead atoms, identical to barium in $BaTiO_3$, and quasinull for the Mg/Nb/Zn/Ti cations, contrarily to the other compounds, in particular, in the PZT 48% (Ref. 1) monoclinic phase.

Whereas in both compounds PMN-PT 35% and PZN-PT 9% the shifts are of the same magnitude, they are not in the same direction: in PMN-PT 35% they are almost in opposite direction, along $=[205]$ and $=[103]$ (Table II), whereas in PZN-PT 9% the lead atom has a displacement close to [001],

TABLE II. Ferroelectric shifts of lead cations and Mg/Nb/Zn/Ti cation from oxygens barycenter with their directions (closest cubic direction), and polarization calculated with the apparent charges from Hewat (Ref. 15).

Ferroelectric shifts	$BaTiO_3$ 204 K $R3m$ (Ref. 12)	$PbTiO_3$ 295 K $P4mm$ (Ref. 13)	PSN 10 K $R3m$ (Ref. 11)	PZT 48% 20 K Cm (Ref. 1)	PMN-PT 10% 80 K $R3m$ (Ref. 10)	PMN-PT 35% 80 K Pm (This work)	PZN-PT 9% 35 K Pm (This work)
$\delta_{\text{PbBa-O}}$ (Å)	0.10	0.49	0.39	0.52	0.27	0.15	0.14
direction	[111]	[001]	[111]	≈[112]	[111]	≈[205]	≈[001]
$\delta_{\text{Ti/Mn/Zn/NB/Sc}}$-O (Å)	0.18	0.31	0.16	0.27	0.05	0.02	0.03
direction	[111]	[001]	[111]	≈[113]	[111]	≈[−10−3]	≈[301]
P (μC/cm^2)	35	55	55	41	29	10	20
Direction	[111]	[001]	[111]	≈[112]	[111]	≈[103]	≈[304]

but Nb/Zn/Ti cations have a displacement almost at 90°, close to [301]. These differences in directions induce differences in the resulting polarization. Indeed from the ferroelectric shifts δ, we could calculate the polarization in magnitude (Table II), using the apparent charges from Hewat,[15] and calculate its direction (Fig. 1 and Table II). In both compounds the polarization is weaker than in other compounds, especially, for PMN-PT 35%. So this phase that allows the rotation of the polarization from rhombohedral to tetragonal direction is characterized by a weak polarization, a strong deformation of oxygen polyhedra, and weak cationic shifts.

In the framework of this work and the works by Noheda *et al.*, we may ask whether such monoclinic phases exist for all lead-based high piezomorphotropic compounds. In particular, we are now trying to check this assumption in 1/2 1/2 compounds such as PSN-PT 43% that is among the best piezocompounds. Also another important question is the crystallochemical origin of the difference between PZT compounds, which get a *Cm* phase and PMN-PT and PZN-PT compounds, which get a *Pm* phase; is there a possibility to observe a *Pm* to *Cm* change when changing concentration? The question of the lead disorder is also an important question. In their study of PZT (Ref. 1) the authors showed that the monoclinic phase is ''prepared'' by disordered shift of the tetragonal and rhombohedral phases of the compounds with concentrations adjacent to the morphotropic boundaries. We have evidenced such short-ranged monoclinic displacements in the rhombohedral phase of PMN-PT 10% compound[10] that may explain the origin of relaxation in this ferroelectric and relaxor compound. Moreover, the study of the stability of these monoclinic phases with concentration and electric field is an important and huge work that is at its beginning; in particular, the possibility to rotate the direction of polarization from the monoclinic to orthorhombic or other directions is probably a key point for the understanding of the giant response of these materials: it is well known that these materials have to be poled to get such interesting properties. One of the interest of these fundamental studies is their direct connection with technological applications.

During the redaction of this paper an optical study of PMN-PT 33% by Xu *et al.*[16] have reported observation of *m*-monoclinic domains, giving an additional support to our diffraction results.

We would like to thank B. Rieu and Y. Shimojo for their technical assistance during the neutron experiments at LLB and JAERI, respectively.

---

[1] B. Noheda, J. A. Gonzalo, L. E. Cross, R. Guo, S.-E. Park, D. E. Cox, and G. Shirane, Phys. Rev. B **61**, 8687 (2000).

[2] B. Noheda, D. E. Cox, G. Shirane, S.-E. Park, L. E. Cross, and Z. Zhong, Phys. Rev. Lett. **86**, 3891 (2001).

[3] D. E. Cox, B. Noheda, G. Shirane, Y. Uesu, K. Fujishiro, and Y. Yamada, Appl. Phys. Lett. **79**, 400 (2001).

[4] H. Fu and R. E. Cohen, Nature (London) **403**, 281 (2000).

[5] D. Vanderbilt and M. H. Cohen, Phys. Rev. B **63**, 094108 (2001).

[6] S. L. Schwartz and T. R. Shrout, Mater. Res. Bull. **17**, 1245 (1982).

[7] J. F. Berar, *IUCr. Sat. Meeting on Powder Diffractometry* (Toulouse, 1990).

[8] J. Rodriguez-Carvajal, *IUCr. Sat. Meeting on Powder Diffractometry* (Toulouse, 1990).

[9] K. Fujishiro, R. Vlokh, Y. Uesu, Y. Yamada, J. M. Kiat, B. Dkhil, and Y. Yamashita, Jpn. J. Appl. Phys., Part 1 **37**, 5246 (1998).

[10] N. De Mathan, E. Husson, G. Calvarin, J. R. Gavarri, A. W. Hewat, and A. Morell, J. Phys.: Condens. Matter **3**, 8159 (1991).

[11] B. Dkhil, J. M. Kiat, G. Calvarin, S. B. Vakhrushev, G. Baldinozzi, and E. Suart (to be published).

[12] C. Malibert, B. Dkhil, J. M. Kiat, D. Durand, J. F. Bérar, and A. Spasojevic, J. Phys.: Condens. Matter **9**, 7485 (1997); J. M. Kiat, G. Baldinozzi, M. Dunlop, C. Malibert, B. Dkhil, C. Menoret, O. Masson, and M. T. Fernandez-Diaz, *ibid.* **12**, 8411 (2000).

[13] A. W. Hewat, Ferroelectrics **6**, 215 (1974).

[14] R. J. Nelmes, R. O. Piltz, W. F. Kuhs, Z. Tun, and R. Restori, Ferroelectrics **108**, 165 (1990).

[15] A. W. Hewat, J. Phys. C **6**, 1074 (1973).

[16] G. Xu, H. Luo, H. Xu, and Z. Yin, Phys. Rev. Rapid Comm. **64**, 020102 (2001).