Fragile morphotropic phase boundary and phase stability in the near-surface region of the relaxor ferroelectric (1−x)Pb(Zn_{1/3}Nb_{2/3})O_{3}-xPbTiO_{3}: [001] field-cooled phase diagrams

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We have examined the effects of field cooling on the phase diagram of the relaxor system (1-x)Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$-xPbTiO$_3$ (PZN-xPT) for compositions near the morphotropic phase boundary (MPB). High-resolution diffraction measurements using Cu K$_\alpha$ x-rays, which probe ≈ 3 μm below the crystal surface, were made on field-cooled (FC) single crystal specimens of PZN-4.5%PT and PZN-6.5%PT under electric fields of 1 kV/cm and 2 kV/cm applied along [001] and combined with previous neutron diffraction data, which probe the entire crystal volume for FC PZN-8%PT [Ohwada *et al.*, Phys. Rev. B **67**, 094111 (2003)]. A comparison to the zero-field-cooled (ZFC) PZN-xPT phase diagram reveals several interesting features: (1) the short-range monoclinic phase observed in the ZFC state on the low-PT side of the MPB is replaced by a monoclinic M_A phase; (2) field cooling extends the tetragonal (*T*) phase to higher temperatures and lower-PT concentrations on field cooling; (3) the orthorhombic (*O*) phase near the MPB is replaced by a monoclinic M_C phase; (4) the vertical MPB in the ZFC phase diagram bends significantly towards the low-PT side in the FC state. These results demonstrate that both

24 the phase stability and the nature of the MPB in PZN-PT within the near-surface regions are

25 fragile in the presence of electric fields.

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I. INTRODUCTION

28   Piezoelectrics are materials that convert mechanical energy to electrical energy and vice-

29 versa. They are thus of significant importance to medical ultrasound, actuators, sensors, and

30 countless other device applications[1-3]. Amongst such materials, solid solutions of the complex

31 perovskites $Pb(Zn_{1/3}Nb_{2/3})O_3$ and $Pb(Mg_{1/3}Nb_{2/3})O_3$ with $PbTiO_3$ (denoted PZN-xPT and PMN-

32 xPT, respectively, where x indicates the atomic percentage of Ti) are relaxor ferroelectrics that

33 exhibit exceptional piezoelectric properties[2]. In particular, extraordinarily high values of the

34 longitudinal piezoelectric coefficient d_{33} have been reported for PZN-8%PT when an electric

35 field (E) is applied along the pseudocubic [001] direction, reaching values of 2500 pC/N and

36 induced strains $\varepsilon \geq 1.7\%$[2,4]. These values are nearly one order of magnitude larger than those

37 observed for conventional piezoelectric ceramics such as $Pb(Zr_xTi_{1-x})O_3$ (PZT). Yet PMN-xPT,

38 PZN-xPT, and PZT have qualitatively similar temperature-composition phase diagrams: the

39 high-temperature paraelectric phases are all cubic (C – space group Pm3m), and the low-

40 temperature ferroelectric phases are rhombohedral (R – space group R3m) for low x and

41 tetragonal (T – space group P4mm) at higher x[5-7]. The strong piezoelectric properties of these

42 materials have been associated with a very steep morphotropic phase boundary (MPB) that

43 separates the T and R phases[5,6,8]. For this reason, many diffraction studies have been performed

44 with excellent wave vector (q) resolution to try to identify the low-symmetry phase located

45 closest to the MPB on the rhombohedral side and to determine the extent of its stability.

In PZT, monoclinic Cm A (M_A) and Cm B (M_B) phases have been reported that bridge the R and T phases near the MPB for $0.46 \leq x \leq 0.52$[9-11]. The M_A and M_B phases have a unique axis b_m that lies along the [110] direction; the unit cell is doubled and rotated 45° about the c-axis with respect to the primitive C cell[12]. In PMN-xPT, however, the MPB region is also complicated. Monoclinic Pm C (M_C) and M_B phases coexist with R, T, and orthorhombic $Amm2$ (O) phases for $0.30 \leq x \leq 0.37$[5,13]. The M_C phase has a primitive unit cell, with a unique axis b_m oriented along [010]. For PZN-xPT, the existence of an O phase over a narrow composition region ($0.09 \leq x \leq 0.11$) has been reported between the R and T phases[6]. The O phase in $BaTiO_3$ can be viewed as a limiting case of the monoclinic M_C phase with $a_m = c_m$[14]. Uesu et $al.$ also observed an M_C phase (i.e., $a_m \neq c_m$) in the ground state of one PZN-9%PT crystal, however two others exhibited a stable O phase[15]. Since the seminal discovery of an intermediate monoclinic phase in PZT[10,16], the zero-field-cooled (ZFC) temperature-composition phase diagrams of these other lead-oxide perovskite ferroelectric relaxors have been revised[5,6,10,11,13].

Generally, an applied electric field (E) will alter the free-energy landscape and thus the various possible polar phases in the vicinity of the MPB[17]. Recently, Tan et $al.$ [18] reported that the MPB of annealed, lead-free $(Bi_{1/2}Na_{1/2})TiO_3$-$BaTiO_3$ can be created, destroyed, or even replaced by another MPB, via phase transitions induced by poling. Moreover, Cao et $al.$[19] have constructed field-cooled (FC) temperature-composition phase diagrams for PMN-xPT for E applied parallel to [001] and [110]. These FC diagrams revealed two interesting features: (i) the presence of a pseudocubic region of abnormal thermal expansion ($c \neq a$) above the dielectric maximum, where the stability range extends to higher temperatures than in the ZFC state; and (ii) a change in the shape of the MPB in the FC state, i.e., the stability of the T phase is extended to $x=0.25$ in the [001] FC state, and it is replaced by an O phase in the [110] FC state[19]. For

69   PZN-8%PT, Ohwada *et al.*[20] reported the phase transition sequence $C \rightarrow T \rightarrow M_C$ on cooling from

70   550 K to 300 K in an electric field E // [001]. Compared with the ZFC diagram[6], it was found

71   that the $C \rightarrow T$ Curie temperature (T_C) in the FC state is ~ 20 K higher (when E = 2 kV/cm) than

72   that in the ZFC state, and that the R phase of the ZFC state is replaced by M_C[6,20]. Several neutron

73   and x-ray diffraction studies have been performed to determine the origin of the high

74   piezoelectricity in PZN-xPT by gradually increasing E at fixed temperature, thereby providing a

75   link between the piezoelectric properties and the structural parameters[5,20,21]. However, the

76   underlying mechanism(s) cannot be fully understood without first understanding the structural

77   evolution of the MPB in the FC state.

78   In this paper, we report the results of an x-ray diffraction (XRD) study performed with high

79   resolution on single crystal PZN-xPT compositions located near the MPB in both ZFC and FC

80   states. Our findings are summarized in Figure 1. The open and solid circles represent data

81   reported previously byKuwata *et al.*[22] and La-Orauttapong *et al*[6], respectively. The vertical

82   dotted lines and the shaded region represent the MPB in the ZFC state. The solid squares

83   represent the phase transition temperatures we measured using XRD in the FC state with E = 1

84   kV/cm // [001] together with those previously reported by Ohwada *et al.*[20] (shaded circles). The

85   modified phase diagram demonstrates that the MPB is quite fragile, and can be either destroyed

86   or reconfigured/created by application of E//[001]. The phase diagram also shows that the

87   temperature range for the stability of the T phase is significantly extended by an applied electric

88   field E, and the phase transformation sequences and temperatures are discussed within that

89   context.

90

91   **II. EXPERIMENTAL DETAILS**

92   Single crystals of PZN-4.5%PT and PZN-6.5%PT (provided by Microfine Materials Tech,

93   Singapore) with dimensions of $2\times2\times4$ mm^3 and $2\times0.2\times4$ mm^3, respectively, were cut with

94   {100}faces, and all faces were polished to 0.25μm. Gold electrodes were deposited on the largest

95   top and bottom surfaces, which we designate as (001) faces. Additionally, ferroelectric (non-

96   relaxor) single crystals of PMN-55%PT and BaTiO$_3$ (Shanghai Institute of Ceramics) with

97   dimensions of $3\times3\times0.5$ mm^3 were prepared with the large surface normal oriented along [001]

98   and polished to 0.25μm for use in a contrast experiment. Diffraction measurements were then

99   performed with the scattering vector Q oriented along [001]. Diffraction measurements were also

100   performed along [H00] and [HH0] on the PZN-4.5%PT crystals. For the PZN-6.5%PT crystals,

101   however, after finishing the measurements along [00L] the electrodes were removed using a

102   polishing blanket with 0.25 μm aluminum powder; new electrodes were then created by applying

103   silver paint to one pair of opposing faces perpendicular to the original (001) faces. Diffraction

104   measurements were then performed using a Philips MPD high-resolution system, which is shown

105   schematically in figure 2 (a). An incident monochromatic x-ray beam was produced by a line-

106   focus x-ray source together with a two-bounce hybrid monochromator using Ge (220) crystals.

107   The system was equipped with an open three-circle Eulerian cradle, which enabled samples to be

108   rotated (φ movement), tilted (ψ movement), and rocked (ω scans). A domed hot-stage was

109   mounted on the cradle, and the temperature was computer controlled. A Ge (220) cut crystal was

110   used as analyzer in which the diffracted beam undergoes three reflections within the groove

111   before entering the detector. The x-ray beam size was chosen to be 3×3 mm^2, and the wavelength

112   was that of Cu K$_\alpha$ = 1.5406 Å. The x-ray generator was operated at 45 kV and 40 mA. Under

113   these conditions, the instrumental wave vector resolution at (200) is 0.0068 degrees in 2θ full-

114   width at half-maximum (FWHM). The lattice parameters were obtained from radial (ω-2θ) scans

measured across the (002), (200), and (220) Bragg peaks. All of these scans were performed using an angular step size of 0.002°and an integration time of 2s. To determine the domain configurations, reciprocal-space mesh scans (RMS) were measured around the (002) and (200) or (020) Bragg peaks in the (H0L) or (0HL) zones, and around (220) in the (HHL) zone. These were generated by performing a sequence of ω-2θ scans at different ω offsets using a step size of 0.01° with an integration time of 0.5s (see figure 2 (b)) and are shown as intensity as a function of reciprocal lattice position (in rlu). Each measurement cycle began by heating to 600 K to anneal the crystals in order to decrease the internal strain[23]; measurements were subsequently taken on cooling. At 520 K, the cubic lattice constant for PZN-6.5%PT is a = 4.054 Å; the corresponding cubic reciprocal lattice unit (or 1 rlu) is a^* = $2\pi/a$ = 1.550 Å^{-1}. All reciprocal-space mesh scans shown here are plotted in reciprocal lattice units.

We note that the x-ray penetration depth (1/e) due to absorption in these PZN-xPT crystals at (200) is only ~ 2.6 μm[24], i.e, our diffraction measurements probe only the near-surface region. Normally, this is more than sufficient to determine the bulk structure of most materials. However, this is not the case for relaxors. An anomalous skin effect spanning the top most 50 μm to 100 μm of the crystal surface has been reported in single crystals of PZN-xPT, PMN-xPT, and $Na_{1/2}Bi_{1/2}TiO_3$ (NBT) in which the near-surface crystal structure differs from that of the bulk[25-27]. This is an extremely important point because the small x-ray penetration depth means that the majority of the x-rays scatter from just the first one or two microns of the crystal surface, and this will produce variability in the diffraction peak profiles and lattice parameters. We will discuss this issue further in the following sections.

In order to investigate the surface domain configuration of PZN-xPT, Piezoresponse Force Microscope (PFM) measurements were also performed using an Atomic Force Microscope

138 (AFM, Bruker multimode 8) with an open loop controller and a conductive AFM tip (MESP-RC,

139 Co/Cr coating, 35 nm tip radius) under contact mode. Temperature control between 300 K and

140 520 K was obtained using a Bruker Multimode heater stage with an accuracy of 0.5 °C.

141

III. PHASE TRANSITIONS, LATTICE PARAMETERS, AND PHASE DIAGRAMS

144 Figure 1 displays the composition-temperature phase diagram for both ZFC and FC (E =

145 1kV/cm) conditions and summarizes the main results of this study. To obtain a more detailed

146 picture of how the phase transitions in PZN-xPT are affected by an electric field, x-ray

147 measurements were performed on cooling under electric fields of E = 0, 1, and 2 kV/cm applied

148 parallel to [001]. The resulting electric field-temperature phase diagrams determined for PZN-

149 4.5%PT and PZN-6.5%PT are summarized in Figure 3. The transition temperatures were

150 determined by following the evolution of the lattice parameters and peak profiles. Details of the

151 XRD measurements and data analysis are given in the next sections.

A. Phase transitions and lattice parameters in ZFC PZN-xPT

153 The ZFC lattice parameters were measured by heating the crystal to 600 K, annealing for 30

154 minutes, and then performing radial scans through the pseudocubic (200) and (220) Bragg peaks

155 on cooling. Data from scans measured at five different temperatures are shown in Figure 4 for

156 PZN-4.5%PT. Two surprising features are immediately evident: (1) the Bragg peak profiles are

157 asymmetric in the cubic phase, particularly for (200); and (2) the Bragg peaks broaden markedly

158 on cooling into the purported T phase. The peak asymmetry is unexpected because it is absent in

159 radial scans measured using the identical x-ray set-up in the cubic phases of single crystal

160 specimens of $BaTiO_3$ and PMN-55%PT, neither of which is a relaxor (see Fig. 11). The

161 asymmetry is therefore a real effect and indicates the presence of a significant lattice gradient

162 (strain) within the near-surface region of the relaxor ferroelectric crystals. This finding is

163 consistent with the previous studies of the anomalous skin effect in PZN-xPT[23] and PMN-xPT[25]

164 mentioned earlier. In particular, the neutron study by Conlon *et al*. on pure PMN found that the

165 lattice parameter varies as a function of depth measured from the crystal surface over a range of

166 order 100 μm[28]. The broadening of the Bragg peaks on cooling is equally unexpected because it

167 indicates that no long-range ordered (LRO) phase transitions take place in this material in the

168 ZFC state over this temperature range within the crystal volume probed by the x-ray beam. The

169 broadening Bragg peaks is discussed in Sec.IV.

170   For PZN-4.5%PT, evidence of a short-range-ordered T-like phase is apparent near 420 K by

171 the Gaussian fit in the left column of Fig. 4 at 400K. On further cooling, a continued coexistence

172 of C and T-like phases is observed until a transition into a new structure occurs near 380 K.

173 Interestingly, PZN-4.5%PT exhibits a T-like phase only in the presence of a coexisting C phase.

174 The a-domains of the T-like phase are not apparent along the (002) zone. The tetragonal c-

175 domain nucleation and growth in the C-phase has also been observed in a new generation of

176 relaxor ferroelectric single crystals[29], where the tetragonal a-domains were observed only on

177 further cooling. The T-like diffraction features are discussed in Sec. IV (see Fig.10). The c-axis

178 lattice parameter for the T-like phase is shown in Fig. 5, but the a-axis lattice parameter could not

179 be determined. Ohwada *et al*. performed neutron diffraction measurements on PZN-8%PT and

180 concluded that the ZFC structure at low temperature is not R[20], as had previously been accepted[6].

181 Subsequent high-energy x-ray studies by Xu *et al*. on PZN[26], and high-resolution neutron studies

182 by Gehring *et al*[30] on PMN-10%PT, also showed that the low temperature bulk phase is not R.

183   As the true ground state bulk crystal symmetry was unknown, the bulk phase was named phase

184   X[19], which designates a distorted structure within an average cubic phase[20].

185   According to the accepted zero-field PZN-xPT phase diagram[6,22], one expects a transition to

186   a LRO R phase for PZN-4.5%PT below ~ 400 K. Assuming a multi-domain sample, this should

187   manifest itself as a narrow single peak at (200) and two sharp peaks at (220). However, from

188   Fig.4 we see that at 385 K the pseudocubic (200) peak profile remains extremely broad and

189   continues to exhibit a weak, secondary peak on the low-angle side, both of which are

190   inconsistent with a LRO R phase. But on cooling to 350 K and then to 300 K the (200) peak

191   profile becomes increasingly better described by a single broad peak. At the same time, the

192   (220) peak profile gradually exhibits an increasingly stronger peak splitting, although it too

193   remains very broad. These data are thus consistent with the gradual formation of a SRO R phase

194   that is limited to the near-surface region in PZN-4.5%PT, which matches the conclusions Xu *et*

195   *al.*[24], who observed a SRO R phase in the near-surface region of PZN-4.5%PT using 10.2 keV x-

196   rays, but a less-distorted (smaller rhombohedral angle) R phase using 67 keV x-rays, which

197   penetrate much deeper into the crystal. The behavior in Fig. 4 is also reminiscent of the x-ray

198   diffraction study of single crystal PZN by Lebon *et al.*[31] who observed that the $C \rightarrow R$ transition

199   occurs gradually between 385 K to 325 K and could be described by the formation of nanometer-

200   sized R domains that grow in number, but not in size, on cooling, thus leading to very broad x-

201   ray diffraction peak profiles.

202   We also performed radial scans at (002); these are shown in the bottom panel (300 K) on the

203   left-hand column in Fig. 4. It can be seen that the positions of the $(200)_C$ and $(002)_C$ Bragg peaks

204   do not coincide, whereas above 430 K they do. This is possibly due to there being a different

205   surface strain between (200) and (002), which correspond to different faces of the same crystal,

206   or to an undetermined symmetry at the surface layer of relaxors. The resulting lattice parameters

207   are given in Fig.5, which were determined by analyzing the (200) and (002) peak lineshapes. The

208   c–axis lattice parameter increases and the a–axis lattice parameter decreases on cooling,

209   analogous to the temperature evolution of the T lattice parameters. Further details regarding this

210   analysis are provided in Sec. IV. Similar results were obtained for PZN-6.5%PT (data not

211   shown), and the phase transition temperatures agreed well with those of the accepted ZFC phase

212   diagram[6,22].

213

214   **B. Phase transitions in [001] FC PZN-xPT**

215   We now discuss the effects of an electric field on the sequence of phase transitions in PZN-

216   xPT in the FC state. The crystals were initially annealed at 600 K after which fields of $E = 1$ and

217   2kV/cm were successively applied parallel to [001]. The phase transformational sequence in the

218   FC state was then studied on cooling by conducting radial and reciprocal-spacer mesh scans

219   performed close to the pseudocubic (002), (200), and (220) Bragg peaks.

220   For PZN-4.5%PT under E=1kV/cm, the phase transformational sequence is

221   $C{\rightarrow}T{\rightarrow}M_C{\rightarrow}M_A$, where the M_C phase coexists with the T phase over a narrow temperature

222   range. At $E = 2$kV/cm, the transformational sequence changes to $C{\rightarrow}T{\rightarrow}M_A$. The difference in

223   these two sequences indicates that the left side of the MPB in the FC state is located near x=4.5

224   for moderate E field. Figure 6 shows the evolution of the pseudocubic (200) Bragg peak profiles

225   with temperature for (a) $E = 1$ kV/cm and (b) 2kV/cm. At high temperatures, the system is cubic,

226   thus the (200) peak is not split; but the lattice parameter determined from (002) radial scans (data

227   not shown) is always slightly larger than that determined from (200) radial scans (see Fig.9 a).

228   On cooling, the crystal structure transforms to T near 440 K for E=1kV/cm and 445 K for

229   E=2kV/cm.   However no T-related splitting of either the (200) or (002) Bragg peaks was

230   observed ostensibly because the field-cooling process produced a predominantly single-domain

231   state. This is evident from the reciprocal-space mesh scans shown in Figs.7 (a-c). For this reason,

232   the c and a-axis lattice parameters were determined from radial scans performed at (002) and

233   (200), respectively. The thermal variation of the lattice parameters is shown in Fig.9 (a).

234   At 380 K and E=1kV/cm, the crystal adopts an M_C (b-domain) phase, which coexists with the

235   T phase. This conclusion is supported by the presence of two peaks in the mesh scan at (220)

236   shown in Fig.7 (f). A tendency of the transverse scan at (200) to split was also observed, even

237   though the contour maps shown in Fig.7 (d) and (e) around (002) and (200) appear to be single

238   peaks. This is presumed to be due to a small volume fraction of M_C. Interestingly, when the

239   sample is heated back up to 520 K and the electric field is increased to 2kV/cm, no evidence of

240   an M_C phase is observed in the mesh scan at (200) and (220) (data not shown). The observation

241   of an M_C (b-domain) phase under E=1kV/cm implies that the left side of the MPB in the FC state

242   is located near x=4.5, as shown in Fig. 1. The disappearance of the M_C b-domains when

243   E=2kV/cm demonstrates that the MPB is fragile because it changes dramatically in the presence

244   of relatively weak applied electric fields. At the same time, the T phase becomes increasingly

245   stable with increasing E//[001]. We note here that the M_C phase component was indexed

246   following the phase transformational sequence of PZN-6.5%PT crystals, but that it was difficult

247   to determine in PZN-4.5%PT.

248   On further cooling, an M_A phase appears near 375 K for both E=1 kV/cm and 2kV/cm, as

249   shown in Fig.6. The appearance of the M_A phase is evident in the reciprocal-space mesh scans

250   (see Figs.7 g-i). The contour maps exhibited a single peak around the (002) zone, revealing that

251   the c axis is fixed along the direction that E is applied. The (200) peak exhibits a splitting along

252 the transverse direction, i.e., $(220) - (\bar{2}20))$ twin peaks. These are the signatures of the M_A

253 domain configuration. However, the contour map around (220) does not reveal the signature

254 triplet splitting of the M_A phase (i.e., one b-domain, containing two a-domains)[19,32], as shown in

255 Fig.7 (i), instead one b-domain and a single a-domain were apparent. This difference might be

256 related to defects in the crystals.

257 For PZN-6.5%PT, a phase transition sequence of $C \rightarrow T \rightarrow M_C \rightarrow M_A$ is found in the FC state,

258 similar to that for x=4.5. However, in this case the M_C phase is stable over a wider temperature

259 range. For E=1kV/cm, the $(002)_C$ peak disappears with decreasing temperature near 440 K and a

260 $(200)_T$ peak develops, demonstrating a $C \rightarrow T$ transformation. Reciprocal-space mesh scans reveal

261 a single domain configuration for the T phase (see Figs.8 a-c). On cooling to 350 K, a $T \rightarrow M_C$

262 phase transition is found (see Figs. 8 d-f). The pseudocubic (220) peak splits into two peaks

263 along the transverse direction; whereas, the (002) remains a single peak. Interestingly, a single

264 domain is observed around (200) and (020), which is discussed in detail in section IV. The M_C

265 symmetry is also evident in the temperature evolution of the lattice parameters (see Fig.9 b). The

266 b-axis lattice parameter in the M_C phase decreases continuously with temperature following the

267 a-axis parameter in the T phase[32]. In the ZFC state, it is worth noting that the MPB lies over a

268 narrow compositional range of 9%<x<11%. However, in the FC state, the M_C phase was clearly

269 present near x=6.5 over a wide temperature range. This difference demonstrates that the

270 application of an electric field along [001] bends the MPB over towards the low PT side of the

271 phase diagram.

272 A third transition to an M_A phase is observed on cooling to 310 K. As shown in Figs.8 (g-i),

273 the pseudocubic (200) peak splits into two peaks along the transverse direction (i.e., $(220) -$

274 $(\bar{2}20)$ twin peaks), the (220) peak splits into three peaks (i.e., one b-domain (020) peak and two

275 a-domains $(200) - (\bar{2}00)$ peaks), and the (002) peak remains a single peak with the c-axis fixed

276 by the direction along which E is applied. This domain configuration is well described by the M_A

277 cell in which a_m and b_m lie along the tetragonal $[\bar{1}\bar{1}0]$ and $[1\bar{1}0]$ directions, and c_m is close to the

278 [001] axis[16].

279

280 ### C. Lattice parameters for [001] FC PZN-xPT

281 To clarify the effects of an electric field on the phase transition sequence in PZN-xPT, the

282 temperature dependences of the lattice parameters for both PZN-4.5%PT and PZN-6.5%PT

283 crystals in the FC state for E=1kV/cm are shown in Fig.9. The cubic lattice parameters for both

284 compositions were determined from radial scans measured at (002) and (200). It can be seen that

285 the values agree well with each other. The tetragonal lattice parameters (a_T, c_T) were extracted

286 from the $(200)_T$ and $(002)_T$ peaks, respectively and cross-checked with scans measured at $(220)_T$.

287 As expected, the tetragonality (c/a-1) becomes more pronounced with decreasing temperature.

288 Because only one of the b-domains in the M_C phase is observed for PZN-4.5%PT, not all of

289 the lattice parameters could be determined (see Fig.9 a). For PZN-6.5%PT the $(002)_T$ peak

290 abruptly shifts to higher 2θ values at 350 K, indicating that the c-axis contracts at the $T{\rightarrow}M_C$

291 transition, whereas the $(200)_T$ peak remains a single peak, corresponding to the b-domain

292 $(020)_{MC}$, and shifts continuously to higher 2θ values with decreasing temperature (see Fig.9 b).

293 The $(220)_T$ peak splits into two peaks along the transverse direction: $(220) - (\bar{2}20))$ twin peaks,

294 from which the values of a_m and the monoclinic angle β_C can be extracted.

295 On cooling to 300 K, both PZN-4.5%PT and PZN-6.5%PT transform into the M_A phase. The

296 c–axis lattice parameter in the M_A phase was calculated from the pseudocubic (002) radial scans

297 and the monoclinic angle β_A. The lattice parameters a_M and b_M were extracted from (220) radial

298   scans. For PZN-4.5%PT, the b–axis lattice parameter of the M_A phase exhibits a discontinuous

299   change at the transition, which was unlike that for PMN-xPT, where $b_M/\sqrt{2}$ and a_T continuously

300   decrease with decreasing temperature[33].

301

302   **IV. DISCUSSION**

303

304   The study of the ground state and the diffraction peak profiles in relaxors in the ZFC state

305   using x-ray diffraction methods began with our attempts to study the phase transitions and MPB

306   in the FC state. During these measurements, we noted a significant asymmetry in the diffraction

307   profiles in the cubic phase near the Curie temperature in the ZFC state. As shown in Fig. 4, the

308    $(200)_C$ and $(002)_C$ Bragg peaks always exhibit an asymmetric lineshape, even at temperatures

309   well above the Curie temperature. This asymmetry is well-described by a very broad peak at low

310   2θ that coexists with a sharp peak at higher 2θ, and it increases on cooling towards the purported

311    $C{\rightarrow}T$ transition temperature. Both of these observations can be understood by the existence of a

312   near-surface region, or "skin," of the crystal that has a depth-dependent lattice spacing, i.e. a

313   lattice gradient that spans at least several microns, which is consistent with the anomalous

314   relaxor skin effect[39]. A comparison of the ZFC and [001] FC diagrams of PZN-xPT in Fig. 1

315   reveals several interesting findings: (i) that the initial R (or M) phase of the ZFC state is replaced

316   by an M_A phase in the FC state; (ii) that the initial O phase in the ZFC state is replaced by an M_C

317   phase in the FC state; (iii) that the MPB in the ZFC diagram, which is nearly vertical and located

318   near 8%<x<11%, is destroyed/created in the FC state by modest fields of E=1 kV/cm and

319   2kV/cm; and (iv) that the stability of the T phase is extended to lower PT compositions and

320   higher temperatures by the application of an electric field.

321

A. Asymmetric diffraction profiles and phase coexistence at high temperature

(i) Near the Curie temperature in the ZFC state

Figure 10 (a) shows the temperature dependence of the $(002)_C$ Bragg peak profile for ZFC PZN-4.5%PT. One can see that the peak intensity decreases discontinuously and the peak width broadens substantially near 420 K. Figure 10 (b) shows representative diffraction peak profiles at 500 K, 400 K, and 300 K. A fit of the $(002)_C$ Bragg peak at 500 K to a single Gaussian function shows that the profile is not symmetric: it exhibits a weak shoulder on the low angle side, which is consistent with the presence of a near-surface lattice gradient as reported by Conlon *et al*[28]. This asymmetry becomes far pronounced at 420 K. Therefore, below 420 K, the $(002)_C$ peak profiles were fit using two Gaussian peaks to test the possibility that the low-angle shoulder might be the result of a coexistence of a weak (low volume fraction) *T*-phase and a strong *C*-phase. However, on cooling to 380 K, a broadened peak is obtained, which we fit to a single Gaussian peak. The temperature dependence of the FWHM is given in Figure 10 (c). The large FWHM indicates that the *T* phase is not LRO and instead consists of SRO regions. We speculate that these SRO tetragonal regions coexist in a cubic matrix around the Curie temperature. After cooling in an electric field $E = 1$kV/cm, a well-defined LRO *T* phase is observed and manifested by the presence of tetragonal c-domains along [001] and a-domains along [100] (radial scans not shown in Fig. 10, but the lattice parameters are given in Fig. 9). Furthermore, recently a distinct tetragonal diffraction profile in the FC state with E//[001] was observed in a single crystal of the related relaxor ferroelectric system $Pb(In_{1/2}Nb_{1/2})O3-Pb(Mg_{1/3}Nb_{2/3})O_3-PbTiO_3$ (PIN-PMN-PT)[29]. Short-range-ordered tetragonal regions may cluster together and grow into a conventional long-range order phase under application of an *E*-field[29].

344   Relaxor ferroelectric single crystals of PMN-xPT and PZN-xPT are known to possess a
345   surface layer ~ 100 μm thick that is structurally distinct from the bulk, a phenomenon known as
346   the anomalous skin effect[34,35]. The internal strains in these materials, which persist even after
347   annealing at high temperature, will result in a d-spacing gradient, that could produce a broadened
348   and asymmetric x-ray diffraction profile[26,34,36]. Given that the absorption-limiting penetration
349   depth (1/e) of Cu Kα x-rays is about 2-3 μm in PZN-xPT[13,37], the most likely explanation for the
350   asymmetric diffraction peak profiles in the cubic phase and the broad, T-like diffraction feature
351   in the cubic matrix is the skin effect, as the low-energy x-rays used here will scatter
352   predominantly from the first one to two microns of the crystal surface. Even in the non-relaxor
353   materials SrTiO$_3$ and LaAlO$_3$, a related skin effect has been reported, and a distinct symmetry
354   observed between the surface near region and the bulk[38,39]. Neutrons, by contrast, being charge-
355   neutral particles, are able to penetrate far more deeply than x-rays into crystals; they therefore
356   provide structural information related to the average bulk crystal symmetry. Prior neutron studies
357   have revealed symmetric peak profiles in the bulk of relaxor PZN-xPT crystals[40]. Hence the
358   difference between neutron and x-ray diffraction profiles highlighted in this study provides
359   evidence that the asymmetric peaks likely result from this skin effect. Furthermore, Ohwada et
360   al. studied the c-axis lattice variation using both neutron and x-ray techniques during the R-M_A-
361   M_C phase transition sequence, and they found a sharp jump in the c-axis lattice spacing using x-
362   rays that was not reproduced by neutron methods[36]. The difference between the diffraction
363   features in the near-surface and bulk regions of the crystal suggest the presence of a non-uniform
364   strain distribution within the skin. In the present study, even under an applied electric field E, we
365   observe a notably asymmetric diffraction profile in both the high and room temperature phases,

366   as shown in Fig.6, which differs from the findings obtained from neutron diffraction. This is also

367   consistent with the idea that the asymmetric diffraction profile is due to the skin effect.

368   In order to further elucidate the skin effect, additional diffraction measurements were made

369   of $(200)_C$ Bragg peaks in single crystals of the conventional non-relaxor ferroelectrics $BaTiO_3$

370   and PMN-55%PT in the cubic phase, as the asymmetric peak broadening is a measure of the

371   strain distribution in the surface layer of relaxors[13,23,36]. The intensity of each diffraction peak is

372   normalized to a value of 100 and plotted on a linear scale, as shown in Fig. 11. From these data it

373   can be seen that the size and strength of the diffraction peak asymmetry in the relaxors is much

374   larger than that in non-relaxor ferroelectric crystals. These findings demonstrate that the relaxor

375   PZN-4.5%PT and PZN-6.5%PT crystals possess a significant skin effect.

376   Piezo-force microscopy (PFM) is an intrinsically surface-sensitive technique, and so it cannot

377   access the interior/bulk domain structure of relaxor crystals. Figure 12 (a) shows an AFM image

378   illustrating the surface roughness (10 μm ×10 μm) for a PZN-4.5% crystal. Vertical PFM phase

379   images were then acquired at 400 K, 430 K, and 450 K on heating, as shown in Figs. 12 (b-d). It

380   is interesting to note that ferroelectric domain structural features, which weaken with increasing

381   temperature, are seen that persist to several tens of degrees above the bulk Curie temperature.

382   We note that similar observations have previously been reported for PZN-12%PT[35]. Again, these

383   features can be attributed to strain gradient distributions, unique atomic configurations, and/or a

384   distinct stoichiometry of the surface layer[34,35,41].

385   Diffuse scattering such as Huang scattering, could also give rise to an for asymmetric

386   diffraction profile[42]. However, we argue that diffuse scattering cannot be the cause of the

387   asymmetric diffraction peak profiles observed in our study. In PZN-xPT, the diffuse scattering

388   intensity is orders of magnitude weaker than the Bragg peak intensity, whereas in this study the

389   asymmetry is visible even when the intensity is plotted on a linear scale (see Fig.11). In addition,

390   the reciprocal-space mesh scans (see Figs.7-8, also plotted on linear scale) show no evidence of

391   the well-known butterfly-shaped intensity contours around (200) or the elliptically-shaped

392   contours around (220)[43,44]. For these reasons, we believe that skin effect is the most possible

393   cause of the diffraction peak asymmetry in the cubic phase. The skin effect would also explain

394   why the diffraction peaks broaden below the Curie temperature: Xu *et al*. showed that the size of

395   the structural distortion decreases with increasing distance from the crystal surface in PZN-xPT[24]

396   and PZN[45], thus the very-near surface region of the crystal never achieves long-range order.

397

398   **(ii) Near the $C \rightarrow T$ phase transition region in the FC state**

399   Broadened diffraction peaks are also notable in the vicinity of the $C \rightarrow T$ transition

400   temperature, and are seen in transverse scans of the $(200)_T$ and $(220)_T$ Bragg peaks in PZN-

401   6.5%PT, whereas that for $(002)_T$ exhibits a sharp peak profile, as shown in Figs.8 (a-c). Similar

402   profiles have also been observed in ternary PIN-PMN-PT relaxor crystals. In order to determine

403   the underlying mechanism for this phenomenon, rocking curves (ω scans at fixed 2θ values)

404   were performed around $(002)_T$, $(200)_T$ and $(220)_T$, as shown in Fig.13, where one or more

405   Gaussian functions were fit to each curve. The results show a single peak around $(002)_T$ and

406   doublets around $(200)_T$ and $(220)_T$. The splitting along the *transverse direction* are similar to

407   those found in the M_C phase under application of an electric field E//[001][32]. However, the

408   crystals are unambiguously in the T-phase region, as can be seen from radial scans and the

409   evolution of the lattice parameters with temperature (see Fig.9 (b)). The splitting of the rocking

410   curves around the (200) and (220) peaks in the tetragonal region may be interpreted as evidence

411   that the M_C phase is a "ferroelectric adaptive phase"[46-49]. Under application of moderate E along

412   [001], the polarization vectors of the tetragonal regions will tend to align with the *E* field,

413   however, a fraction of the vectors may remain perpendicular: thus, the domain state is referred to

414   as a pseudo-mono domain configuration. Such polydomain ferroelastic crystals consist of

415   structural twins that accommodate elastic strain[47,50]. Wang has predicted that the twinned *a*- and

416   *c*-domains in the *T*-phase can produce a superlattice of M_C symmetry if they are adaptive[48,49]. In

417   turn, this leads to a splitting in the ω scans along the $(200)_T$ and $(220)_T$ peaks, given as

418
$$\beta_C = 90° + 2A\nu(1-\nu)(\tan^{-1}\frac{c_t}{a_t} - 45°);\qquad\qquad(1)$$

419   where β_C is the angle of the low symmetry M_C phase, *A* is a fitting constant (close to 1), and ν is

420   the volume fraction of the twinned *a*- or *c*-domains. The diffraction broadening feature along the

421   transverse direction in Fig.8 may result from twin-related tetragonal nano-variants, not being

422   perfectly stable with respect to each other in a manner that achieves complete stress

423   accommodation. We note that this feature (i.e., diffraction broadening along the transverse

424   direction) is more profound in a poled PIN-PMN-PT crystal[12], indicating poled relaxor crystals

425   are dominated by nanotwins. These results also provide indirect evidence that the nanotwin

426   boundary is the origin of high piezoelectric properties for relaxor ferroelectric crystals[50].

427

428   **B. Crystal structure at 300 K**

429   As shown in Fig. 4, the $(002)_C$ and $(200)_C$ Bragg peaks at 300 K are significantly different,

430   much more so than in the high temperature region. As a result, the difference between the *a*- and

431   *c*-axis lattice parameters determined from the $(200)_C$ and $(002)_C$ peaks is notably larger than the

432   experimental errors (see Fig. 5). These findings show that the ground state for PZN-4.5%PT is

433   not a long-range ordered *R*-phase (nor is that for PZN-6.5%PT, data not shown). This is

434   inconsistent with previous observations by single crystal and powder diffraction, via low and

435 high energy x-ray beams[6,25]. Our findings are similar to those for PZN-8%PT reported by

436 Ohwada *et al.*, where an unknown ground state designated as "phase X" was conjectured. Also

437 puzzling was the difference between the peak intensities at $(200)_C$ and $(002)_C$ and whether or not

438 this difference was intrinsic. The *d*-spacings were determined by the positions of the diffraction

439 peaks, which can be influenced by the surface condition (i.e., $(200)_C$ and $(002)_C$): such as

440 mechanically-induced stain, defect or stoichiometric inhomogeneity[23]. However, before each

441 measurement, the crystals were annealed above 600 K for 30 mins to relax the residual surface

442 strain. Interestingly, the intensity and FWHM of the $(002)_C$ and $(200)_C$ peaks exhibited

443 differences above the Curie temperature (see Fig.4 at 430 K), the difference increased with

444 decreasing temperature (i.e. as the *c*-lattice increased, and the *a*-lattice decreased).

445 In addition to the difference between the diffraction intensities at $(002)_C$ and $(200)_C$, the peak

446 profiles were highly asymmetric, as can be seen from the one-peak Gaussian mode fits shown in

447 Fig. 10 (b). This asymmetry indicates that additional peaks may exist within the broad one, but

448 were hard to distinguish. We note that the asymmetry of the $(200)_C$ peak is consistent in peak

449 position ranges with the $(002)_C$ (see Fig.4). We thus could speculate that the ground state might

450 be a monoclinic phase, rather than the distorted cubic "phase X" as proposed by Ohwada *et al*.

451 The FWHM of the $(200)_C$ diffraction peak is much larger than expected given the resolution

452 of the Ge (220) cut crystal analyzer (see Fig. 10 c). The large FWHM most likely results from a

453 collection of micro-crystal boundaries contributing to the total scattering intensity[26]. An

454 explanation for this broadening nature has conventionally been a skin effect, which is known to

455 effect x-ray studies of relaxor crystals due to the limited x-ray penetration depth[26]. The neutron

456 study of both powder and single crystal samples of PMN-xPT by Phelan *et al.*[13] has shown that

457 the skin effect vanishes on the tetragonal side of the MPB, i.e. for Ti concentrations x ~ 0.40 and

458 higher.   They presented a revised PMN-xPT phase diagram where the ground state was

459 designated as "short-range R/M"[13]. Analogously, the ground state of PZN-xPT on the left side of

460 the MPB was indexed as a SRO monoclinic structure because they share similarly broadened

461 features. During a manuscript revision, Zhang et al.[10] found experimental evidence that a LRO R

462 phase coexists with both LRO and SRO monoclinic regions on the Zr-rich side of the MPB of

463 PZT. These findings indicate the ground state of these relaxor solid solutions may be more

464 complex than previously thought.

465

466   **C. Extension of the *T* phase region by E**

467   It was found that the stability of the *T* phase is significantly enhanced by the application of an

468 electric field *E* for single crystals of PZN-xPT with x=4.5% and 6.5%, compositions that lie on

469 the left side of the MPB. Even though PZN-xPT crystals with x>9% (i.e., located on the right

470 side of the MPB) were not studied, one can make inferences from the related ternary PIN-PMN-

471 PT relaxor solid crystals, located near the MPB but to the right side. In this case, an *E*-field

472 induced enhancement of the *T* phase stability was clearly observed. We thus believe that this

473 phenomenon is a common feature for all relaxor crystals, and not strongly dependent on

474 compositions.

475

476   **(i) Extension of the T phase to higher temperatures**

477   In order to understand the extension of the *T* phase to higher temperatures (*T*) by the

478 application of an electric field *E*, a simple form of the classical Landau theory was employed.

479 Generally, the free energy (*G*) of the system, being a function of the mole fraction PT (*x*) and *Γ*,

480   can be described as a symmetry-adapted Landau series with respect to the absolute value of the

481   spontaneous polarization P in the unconstrained state,

482
$$G(x,T,P) = \frac{1}{2}\alpha(x)(T - T_0)P^2 + \frac{1}{4}\beta(x)P^4 + \frac{1}{6}\gamma(x)P^6 - EP;$$
(2)

483   where $\alpha(x)$, $\beta(x)$ and $\gamma(x)$ are the coefficients of the various ordered terms, respectively. E is the

484   normalized externally applied electric field, where it is also assumed that the polarization and E

485   are parallel.

486   Our idea is to determine, in the simplest possible case, the E-field induced extension of the T

487   phase. For a first-order phase transition, one can assume that $\alpha(x)>0$, $\beta(x)<0$, and $\gamma(x)>0$. When

488    $E=0$, $G(P)$ has two minima at $P \neq 0$ in addition to one at $P = 0$. For $T<T_C$, $G<0$, so that a

489   discontinuous transition occurs from $P=0$ into the state with two minima at $P \neq 0$. The

490   paraelectric $\rightarrow$ ferroelectric transition temperature T_C under $E=0$ can then be found as

491
$$T_C = T_0 + \frac{3}{16}\frac{\beta(x)^2}{\alpha(x)\gamma(x)}.$$
(3)

492   From the Clausius-Clapeyron equation ($T_C(E) = T_C - \frac{\Delta P}{\Delta S}E$, where ΔP and ΔS are the

493   discontinuous change in polarization and entropy at T_C), the Curie temperature T_C at various E is

494
$$T_C(E) = T_C + \frac{4}{\alpha(x)}\sqrt{\frac{-\gamma(x)}{3\beta(x)}}E.$$
(4)

495   From Eq. (4), it is obvious that T_C increases with increasing E field when $\alpha(x)>0$. This

496   prediction that the T phase is extended by E applied parallel to [001] is a common characteristic

497   of all $T{\rightarrow}C$ transition that are 1st order, independent of the composition and the category of the

498   crystals.

499

500   **(ii) Extension of the T phase to lower x**

501   As shown in Fig. 4, the coexistence of T and C phases was only found for PZN-4.5%PT

502   crystals in the ZFC state, where a $C \rightarrow$ SRO monoclinic transformation occurred on cooling.

503   However, for [001] PZT-4.5%PT crystals in the FC state, the T-phase existed independently of C

504   (see Fig. 6). This demonstrates that the T-phase can be extended to lower PT contents under E.

505   In the PZN-xPT solution, substitution of the $[TiO_4]^{4-}$ octahedron for the more complex

506   $[Zn_{1/2}Nb_{2/3}O_4]^{4-}$, results in an MPB separating R and T ferroelectric phases. The c/a ratio of the

507   T-phase weakens with decreasing x on approaching the MPB. PZN-4.5%PT can be considered as

508   a special composition in the diagram, where a gradual transition between T microdomains in a C

509   matrix and a macroscopic T phase begins to occur. If the T microdomains are much smaller than

510   the coherence length of x-rays, the average structure appears monoclinic or X by diffraction in

511   the ZFC state. However, in the FC state, the T microdomains align parallel to E, and thus a

512   macroscopic T phase is observed to sandwich the C and M_A ones on cooling.

513

514   **D. Destruction of old and creation of new MPB by E**

515   The most significant feature in Figure 1 is the destruction of the R/M and T MPB of the ZFC

516   state by a moderate E and creation of a new one. PZN-4.5%PT and PZN-6.5%PT undergo a

517   transformational sequence $C \rightarrow T \rightarrow M_C \rightarrow M_A$. This sequence is similar to that previously reported

518   for PZN-8PT by Ohwada *et al*., except the present results reveal that the $M_C \rightarrow M_A$ transition is

519   decreased to room temperature by E.

520   In the ZFC state, the transformational sequence is $C \rightarrow T \rightarrow R$ or M for x<8%, while the

521   transformational sequence is $C \rightarrow T$ for x>11%. In the ZFC state, a MPB exists for 8%<x<11%,

522   which is nearly vertical separating R or M and T phases. However, under E//[001], a structurally

523   bridging M_C phase is found near the MPB; and in particular, the vertical nature of the MPB was

524 transformed in the *x-T* field to being notably bent towards the lower *x* side. This M_C phase

525 appeared not only in the range of the MPB of the ZFC state of 8%<*x*<11%, but also over an

526 extended range of 4.5%<*x*<8%. To understand the tilting of the MPB, it is worth referring to the

527 polarization rotation path of PZN-xPT for *E*//[001] as the polarization rotation path depends on

528 x. The bifurcated path indicates that the lowest free energy path for the various compositions is

529 different. Analogously, we conjecture that the lowest free energy path is also different in the

530 cooling process without (i.e., ZFC state) and with (i.e., FC state) an *E* field applied to a constant

531 composition, and for different compositions in the FC state. For PZN-6.5%PT, the polarization

532 rotation path is along $T{\rightarrow}R$ in the ZFC state, while in the FC state, the polarization first rotates

533 along the $T{\rightarrow}O$ path, and then abruptly jumps to $T{\rightarrow}R$ one. This results in a modified phase

534 transition sequence of $T{\rightarrow}M_C{\rightarrow}M_A$. Whereas, for low PT crystals (i.e., x<4.5%), the

535 polarization rotation path is along $T{\rightarrow}R$ in both ZFC and FC (e.g. moderate amplitude of

536 *E*=1kV/cm) states.

537

538   **E. Atypical M_C Domain configurations in FC PZN-6.5%PT**

539   Monoclinic symmetry allows for 24 possible domain states and thus normally results in very

540 complicated domain configurations. However, in PMN-PT and PZN-PT crystals, an applied

541 E//[001] fixes the *c* axis, simplifying the configuration. The resultant signature polar vector

542 orientation and domain configuration for the M_C phase are schematically illustrated in Fig.14 (a).

543 In the H0L plane, there are only two *b* domains that are related by a 90° rotation about the *c* axis,

544 where each of these has two related *a* domains having an angle of *β* or 180-β with c_m. The

545 polarization vectors of each of these four domains is rotated under *E* in the monoclinic plane,

546 forming identical angles along the [001] .

547   An atypical domain configuration was observed in this experiment as shown in Fig.8 and

548   schematically illustrated in Fig.14 (b). As expected, a single peak was observed around the (002)

549   zone, illustrating that the c axis is fixed along the direction that E was applied. However, about

550   the (020) zone, only a single b domain was found that was slightly tilted along the longitudinal

551   direction, rather than containing two a domains in a typical case. Generally, in the M_C phase, the

552   a and b domains can be switched between each other about the c axis, as designated by shaded

553   and unshaded axis labels in Fig.14 (a). In turn, four polar vectors in the $a_m c_m$ plane are possible.

554   However, surface residual stress in the ferroelectric crystals can break this domain equivalence,

555   resulting in some domains being absent compared to the equilibrium configuration.

556

557   **V. CONCLUSIONS**

558   A comprehensive x-ray diffraction study of single crystal PZN-4.5%PT and PZN-6.5%PT

559   was performed on cooling under E=0 kV/cm, 1 kV/cm and 2kV/cm. In the ZFC state, the ground

560   state crystal structure of PZN-4.5%PT resembles a short-range-ordered monoclinic phase or a

561   distorted rhombohedral one due to the skin effect, which is consistent with a previous

562   synchrotron study by Xu et $al.$ on the same compound[24]. It was established that the phase

563   transformational sequence with decreasing temperature for both PZN-4.5%PT and PZN-6.5%PT

564   is $C{\rightarrow}T{\rightarrow}M_C{\rightarrow}M_A$ in the FC state. An [001] FC phase diagram was constructed based on these

565   diffraction data, and it was found that the phase stability and MPB were fragile to application of

566   moderate electric fields. The T phase region was found to be significantly extended by E. In

567   particular, the vertical nature of the MPB in the ZFC diagram was lost.

568

569

580

581   **Figure captions**

582

583   **Figure 1** PZN-xPT phase diagram near the MPB. Open circles represent the data for ZFC PZN-

584   xPT reported by Kuwata *et al.*[22]. Solid circles represent the more recent data for ZFC PZN-xPT

585   reported by La-Orauttapong *et al.*[6] The symbols *R* (or *X*) and *O* designate the rhombohedral (or

586   *X*) and orthorhombic ZFC phases. Our data on FC PZN-4.5%PT and PZN-6.5%PT are plotted as

587   solid squares and included with those of Ohwada *et al*. for FC PZN-8PT (shaded circles). The

588   black dotted lines represent the MPB in the ZFC state, while the red dashed lines represent the

589   MPB in the FC state (E = 1 kV/cm // [001]). Our ZFC results are not shown in this figure (see

590   text), as they agree well with the ZFC results of La-Orauttapong *et al*[7].

591

592   **Figure 2** Schematic diagram of (a) Phillips MPD high resolution x-ray diffractometer and (b)

593   single and reciprocal-space mesh scans in the (H0L) zone. The rocking curve (ω scan) describes

594   a circular arc centered on the origin; the detector scan (2θ scan) follows the circumference of the

595   Ewald sphere; and the ω-2θ radial scan describes a straight line pointing radially from the origin.

596   A typical reciprocal-space mesh scan centered on $(301)_C$ is shown.

597

598

599   **Figure 3** Electric field-temperature phase diagram for (a) PZN-4.5%PT and (b) PZN-6.5%PT in

600   the FC state with E//[001]. Arrows indicate the sequence of phase transitions on cooling. Solid

601   circles represent the respective transition temperatures as defined in the text. Lines are guides to

602   the eyes.

603

604   **Figure 4** Evolution of the pseudocubic $(200)_C$ and $(220)_C$ Bragg peak lineshapes on cooling from

605   the cubic phase to the short-range ordered monoclinic phase for PZN-4.5%PT. Open and solid

606   circles represent the $(200)_C$ and $(002)_C$ peak profiles in the C and short-range-ordered monoclinic

607   phases, respectively. The square root of the diffracted x-ray intensity is plotted in order to make

608   weak peaks and shoulders more visible.

609

610   **Figure 5** Lattice parameters of ZFC PZN-4.5%PT as a function of temperature.

611

612   **Figure 6** Evolution of the pseudocubic (200) Bragg peaks for PZN-4.5%PT cooled under (a) $E =$

613   1 kV/cm and (b) $E = 2$ kV/cm, respectively, where $\boldsymbol{E}$ // [001]. The square root of the diffracted x-

614   ray intensity is plotted in order to make weak peaks and shoulders more visible.

615

616

617   **Figure 7** Reciprocal-space mesh scans centered on the pseudocubic (002), (200) and (220) Bragg

618   peaks at different temperatures for FC PZN-4.5%PT (E = 1 kV/cm // [001]).

619

620   **Figure 8** Reciprocal-space mesh scans centered on the pseudocubic (002), (200) and (220) Bragg

621   peaks at different temperature for FC PZN-6.5%PT (E = 1 kV/cm // [001]).

622

623   **Figure 9** Lattice parameters of FC (a) PZN-4.5%PT and (b) PZN-6.5%PT as a function of

624   temperature (E = 1 kV/cm // [001]). Dashed lines represent the respective transition temperatures

625   as defined in the text. The experimental uncertainty of the lattice parameters extracted from

626    $(002)_C$ and $(200)_C$ is less than 0.001Å.

627

628   **Figure 10** (a) x-ray intensity contour map of the PZN-4.5%PT $(002)_C$ Bragg peak showing the

629   evolution of the width with temperature. (b) Representative $(002)_C$ Bragg peaks at 520 K, 400 K,

630   and 300 K. The data were fit using single-peak and two-peak Gaussian functions, respectively.

631   (c) Temperature dependence of the $(002)_C$ Bragg peak FWHM derived from the Gaussian fits.

632

633   **Figure 11** Profile of pseudocubic $(200)_C$ Bragg peak in the cubic phase for relaxor and normal

634   ferroelectric single crystals: (a) PZN-4.5%PT at 430K, (b) PZN-6.5%PT at 430K, (c) $BaTiO_3$ at

635   430K and PMN-55%PT at 570K, respectively. The intensity of each diffraction peak was

636   normalized in order to clearly reveal the asymmetrical and broadening features.

637

Figure 12 (a) Topography AFM image of the surface roughness of PZN-4.5%PT single crystals of an area of 10×10 μm and (b) the corresponding phase image of PFM of the same region at various temperatures. The surface ferroelectric domain configuration remains identical above the bulk phase transition.

Figure 13 (a) Comparison of rocking curves for FC PZN-6.5%PT in the tetragonal phase.

Figure 14 Polar vectors and domain configurations in cubic Cartesian coordinates for the (a) signature M_C phase and (b) atypical M_C phase observed in this work. The polar vector in the monoclinic M_C phase lies in the a_m-c_m monoclinic plane, as designated by the arrows.

References

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

[2]   S. E. Park and T. R. Shrout, Journal of Applied Physics **82,** 1804 (1997).

[3]   Y. Wang, J. Li, and D. Viehland, Materials Today **17,** 269 (2014).

[4]   D. S. Paik, S. E. Park, S. Wada, S. F. Liu, and T. R. Shrout, Journal of Applied Physics **85,** 1080 (1999).

[5]   B. Noheda, D. E. Cox, G. Shirane, J. Gao, and Z. G. Ye, Physical Review B **66,** 054104 (2002).

[6]   D. La-Orauttapong, B. Noheda, Z. G. Ye, P. M. Gehring, J. Toulouse, D. E. Cox, and G. Shirane, Physical Review B **65,** 144101 (2002).

[7]   D. Phelan, X. Long, Y. Xie, Z. G. Ye, A. M. Glazer, H. Yokota, P. A. Thomas, and P. M. Gehring, Physical Review Letters **105,** 207601 (2010).

661 [8] D. E. Cox, B. Noheda, G. Shirane, Y. Uesu, K. Fujishiro, and Y. Yamada, Applied Physics

662 Letters **79,** 400 (2001).

663 [9] B. Noheda and D. E. Cox, Phase Transitions **79,** 5 (2006).

664 [10] N. Zhang, H. Yokota, A. M. Glazer, Z. Ren, D. A. Keen, D. S. Keeble, P. A. Thomas, and Z.

665 G. Ye, Nature Communications **5,** 5231 (2014).

666 [11] B. Noheda, D. E. Cox, G. Shirane, R. Guo, B. Jones, and L. E. Cross, Physical Review B **63,**

667 014103 (2001).

668 [12] Y. Wang, Z. Wang, W. Ge, C. Luo, J. Li, D. Viehland, J. Chen, and H. Luo, Physical

669 Review B **90,** 134104 (2014).

670 [13] D. Phelan, E. E. Rodriguez, J. Gao, Y. Bing, Z. G. Ye, Q. Huang, J. Wen, G. Xu, C. Stock,

671 M. Matsuura, and P. M. Gehring, Phase Transitions **88,** 283 (2015).

672 [14] B. Jaffe, *Piezoelectric Ceramics* (Academic Press, India, 1971).

673 [15] Y. Uesu, M. Matsuda, Y. Yamada, K. Fujishiro, D. E. Cox, B. Noheda, and G. Shirane,

674 Journal of the Physical Society of Japan **71,** 960 (2002).

675 [16] B. Noheda, D. E. Cox, G. Shirane, J. A. Gonzalo, L. E. Cross, and S. E. Park, Applied

676 Physics Letters **74,** 2059 (1999).

677 [17] A. A. Bokov and Z. G. Ye, Applied Physics Letters **92,** 082901 (2008).

678 [18] C. Ma, H. Guo, S. P. Beckman, and X. Tan, Physical Review Letters **109,** 107602 (2012).

679 [19] H. Cao, J. F. Li, D. Viehland, and G. Y. Xu, Physical Review B **73,** 184110 (2006).

680 [20] K. Ohwada, K. Hirota, P. W. Rehrig, Y. Fujii, and G. Shirane, Physical Review B **67,**

681 094111 (2003).

682 [21] B. Noheda, Z. Zhong, D. E. Cox, G. Shirane, S. E. Park, and P. Rehrig, Physical Review B

683 **65,** 224101 (2002).

684   [22]   J. Kuwata, K. Uchino, and S. Nomura, Ferroelectrics **37,** 579 (1981).

685   [23]   W. S. Chang, M. Shanthi, K. K. Rajan, L. C. Lim, F. T. Wang, C. T. Tseng, C. S. Tu, P.

686   Yang, and H. O. Moser, Journal of Applied Physics **101,** 124104 (2007).

687   [24]   H. Cao, F. M. Bai, N. G. Wang, J. F. Li, D. Viehland, G. Y. Xu, and G. Shirane, Physical

688   Review B **72,** 064104 (2005).

689   [25]   G. Y. Xu, H. Hiraka, G. Shirane, and K. Ohwada, Applied Physics Letters **84,** 3975 (2004).

690   [26]   G. Y. Xu, D. Viehland, J. F. Li, P. M. Gehring, and G. Shirane, Physical Review B **68,**

691   212410 (2003).

692   [27]   W. Ge, C. P. Devreugd, D. Phelan, Q. Zhang, M. Ahart, J. Li, H. Luo, L. A. Boatner, D.

693   Viehland, and P. M. Gehring, Physical Review B **88,** 174115 (2013).

694   [28]   K. H. Conlon, H. Luo, D. Viehland, J. F. Li, T. Whan, J. H. Fox, C. Stock, and G. Shirane,

695   Physical review B **70,** 172204 (2004).

696   [29]   C. Luo, Y. Wang, Z. Wang, W. Ge, J. Li, H. Luo, and D. Viehland, Applied Physics Letters

697   **105,** 232901 (2014).

698   [30]   P. M. Gehring, W. Chen, Z. G. Ye, and G. Shirane, Journal of Physics-Condensed Matter

699   **16,** 7113 (2004).

700   [31]   A. Lebon, H. Dammak, G. Calvarin, and I. O. Ahmedou, Journal of Physics-Condensed

701   Matter **14,** 7035 (2002).

702   [32]   F. M. Bai, N. G. Wang, J. F. Li, D. Viehland, P. M. Gehring, G. Y. Xu, and G. Shirane,

703   Journal of Applied Physics **96,** 1620 (2004).

704   [33]   H. Cao, J. Li, and D. Viehland, Journal of Applied Physics **100,** 034110 (2006).

705   [34]   G. Xu, P. M. Gehring, C. Stock, and K. Conlon, Phase Transitions **79,** 135 (2006).

706   [35]   N. Domingo, N. Bagues, J. Santiso, and G. Catalan, Physical Review B **91,** 094111 (2015).

707   [36]   K. Ohwada, K. Hirota, P. W. Rehrig, P. M. Gehring, B. Noheda, Y. Fujii, S. E. E. Park, and

708   G. Shirane, Journal of the Physical Society of Japan **70,** 2778 (2001).

709   [37]   H. Cao, J.-f. Li, and D. Viehland, Journal of Applied Physics **100,** 084102 (2006).

710   [38]   Chrosch Jutta and E. K. H. Salje, Journal of Physics: Condensed Matter **10,** 2817 (1998).

711   [39]   E. K. H. Salje, M. Alexe, S. Kustov, M. C. Weber, J. Schiemer, G. F. Nataf, and J. Kreisel,

712   Scientific Reports **6,** 27193 (2016).

713   [40]   P. M. Gehring, K. Ohwada, and G. Shirane, Physical Review B **70,** 014110 (2004).

714   [41]   P. Gao, H. J. Liu, Y. L. Huang, Y. H. Chu, R. Ishikawa, B. Feng, Y. Jiang, N. Shibata, E. G.

715   Wang, and Y. Ikuhara, Nature Communications **7,** 11318 (2016).

716   [42]   H. You and Q. M. Zhang, Physical Review Letters **79,** 3950 (1997).

717   [43]   G. Y. Xu, P. M. Gehring, and G. Shirane, Physical Review B **72,** 214106 (2005).

718   [44]   G. Y. Xu, Z. Zhong, Y. Bing, Z. G. Ye, and G. Shirane, Nature Materials **5,** 134 (2006).

719   [45]   G. Y. Xu, Z. Zhong, Y. Bing, Z. G. Ye, C. Stock, and G. Shirane, Physical Review B **67,**

720   104102 (2003).

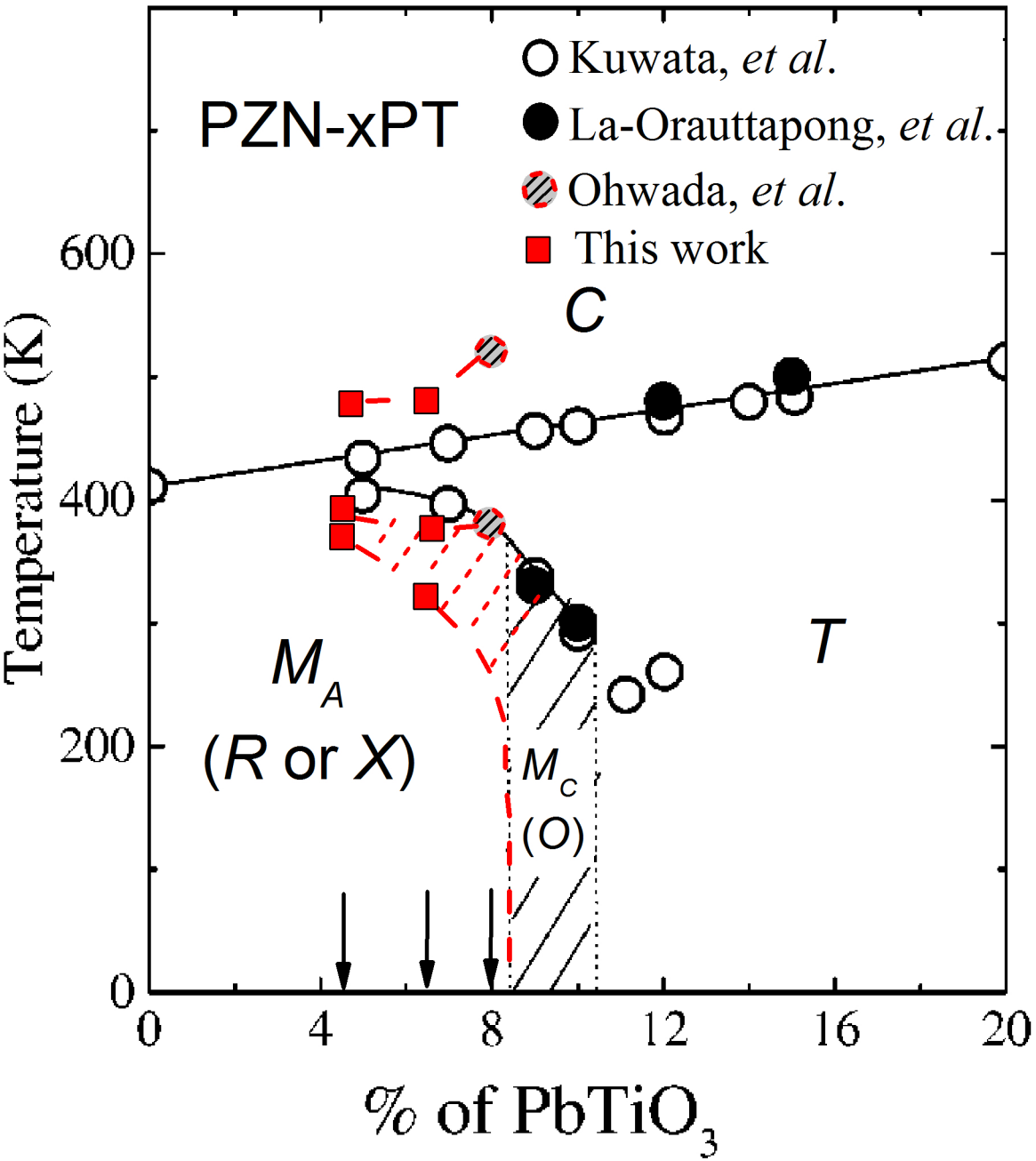721   [46]   D. Viehland, Journal of Applied Physics **88,** 4794 (2000).

722   [47]   Y. M. Jin, Y. U. Wang, A. G. Khachaturyan, J. F. Li, and D. Viehland, Physical Review
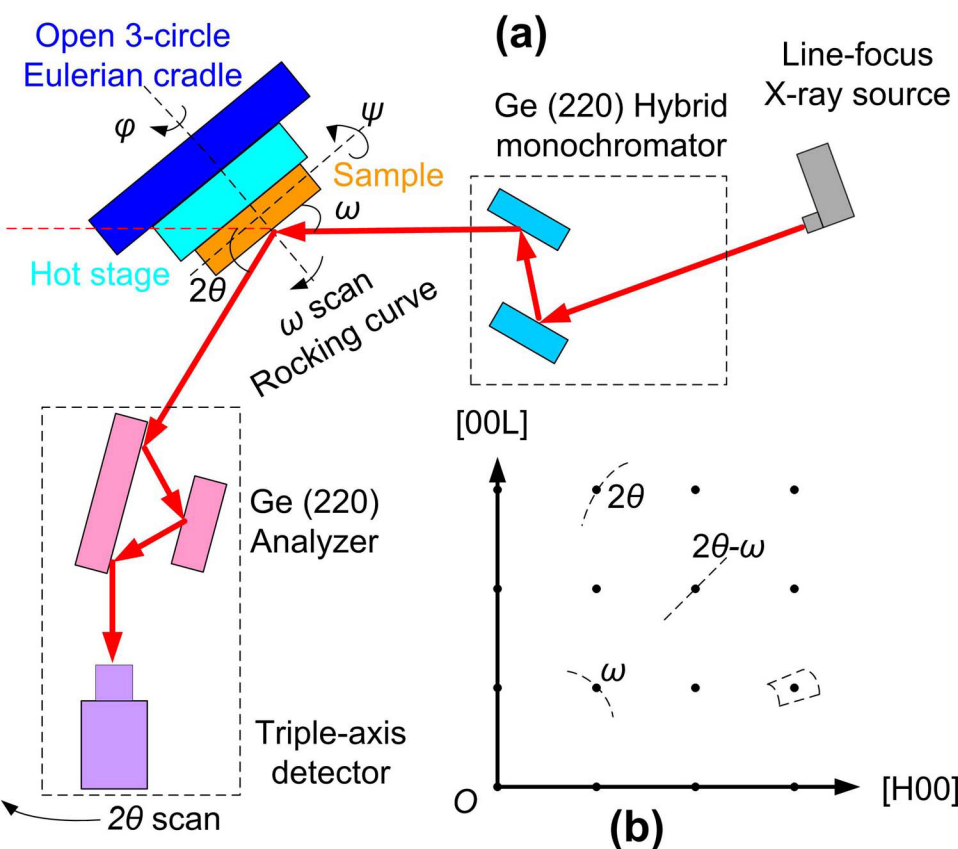
723   Letters **91,** 197601 (2003).

724   [48]   Y. U. Wang, Physical Review B **74,** 104109 (2006).

725   [49]   Y. U. Wang, Physical Review B **73,** 014113 (2006).

726   [50]   D. D. Viehland and E. K. H. Salje, Advances in Physics **63,** 267 (2014).
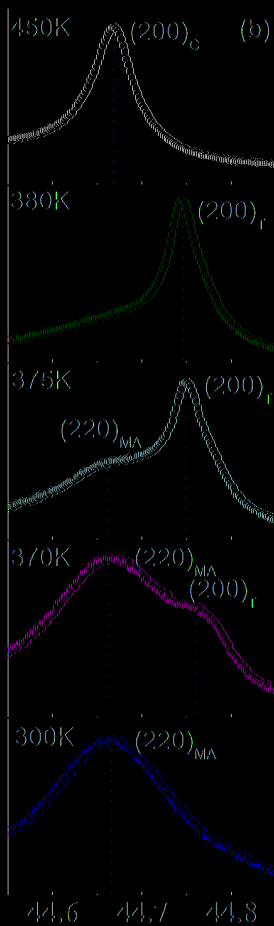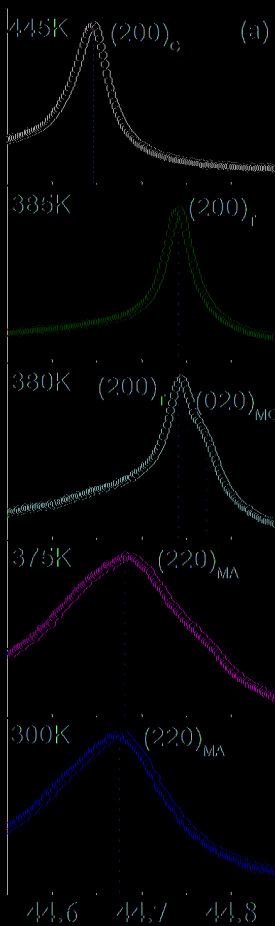
727

Figure: PZN-xPT phase diagram, Temperature (K) versus % of PbTiO₃.

Legend:
- ○ Kuwata, *et al.*
- ● La-Orauttapong, *et al.*
- ◐ Ohwada, *et al.*
- ■ This work

Regions labeled: C, T, M_A (R or X), M_C (O).

(a)

Open 3-circle Eulerian cradle

Line-focus X-ray source

Ge (220) Hybrid monochromator

φ

ψ

Sample

ω

Hot stage

2θ

ω scan Rocking curve

Ge (220) Analyzer

Triple-axis detector

2θ scan

(b)

[00L]

2θ

2θ-ω

ω

[H00]

O

PZN-xPT, FC

(a): PZN-4.5PT

M_A M_C T C

SRM T C

(b): PZN-6.5PT

M_A M_C T C

SRM T C

Electric Field (kV/cm)

Temperature (K)

PZN 4.5PT, ZFC

PZN4.5PT, ZFC

PZN-4.5PT, FC, E//[001]$_c$

PZN-4.5PT, FC, E=1kV/cm

(a)   (002)   **(b)**   (200)   **(c)**   (220)   **390 K**

(d)   **(e)**   **(f)**   **380 K**

(h)   **(i)**   **(j)**   **300 K**

PZN-6.5PT, FC, *E*=1kV/cm

(a)　　(002)　　　　　**(b)**　　　(200)　　　　　**(c)**　　(220)　　**370 K**

(d)　　　　　　　　　　　**(e)**　　　　　　　　　　**(f)**　　　　　　**350 K**

(h)　　　　　　　　　　　**(i)**　　　　　　　　　　**(j)**　　　　　　**300 K**

PZN-xPT, FC, E: 1kV/cm

(a): PZN-4.5PT

(b): PZN-6.5PT

Legend:
- PZN-4.5PT:M_A
- PZN-6.5PT:M_C
- PZN-6.5PT:M_A

Y-axis (top/middle panels): Lattice parameters (Å)
Y-axis (bottom panel): β-90 (°)
X-axis: Temperature (K)

Phase labels: M_A, M_C, T, C

Parameter labels: c_M, $a_M/\sqrt{2}$, $b_M/\sqrt{2}$, a_M, b_M, c_T, a_T, a_c

(a)

(b) 500 K 400 K 300K

(c)

PZN-4.5%PT
430K

PZN-6.5%PT
430K

BaTiO$_3$
430K

PMN-60%PT
560K

Intensity (A.U.)

2θ (Deg)

(002)　　　　　(200)　　　　　(220)

Intensity (A.U.)

ω (Deg)　　　ω (Deg)　　　ω (Deg)

(a)

(b)