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Universal phase diagram for high-piezoelectric perovskite systems

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Strong piezoelectricity in perovskite-type $PbZn_{1-x}Ti_xO_3$ (PZT) and $Pb(Zn_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PZN–PT) systems is generally associated with the existence of a morphotropic phase boundary (MPB) separating regions with rhombohedral and tetragonal symmetry. An x-ray study of PZN–9% PT has revealed the presence of an orthorhombic phase at the MPB, and a near-vertical boundary between the rhombohedral and orthorhombic phases, similar to that found for PZT between the rhombohedral and monoclinic phases. We discuss the results in the light of a recent theoretical paper by Vanderbilt and Cohen [Phys. Rev. B **63**, 94108 (2001)], which attributes these low-symmetry phases to the high anharmonicity in these oxide systems. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1384475]

Ferroelectric perovskite-type materials are of great fundamental and technological importance. Among such materials, $PbZn_{1-x}Ti_xO_3$ (PZT) and $Pb(Zn_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PZN–PT) systems exhibit unusually large piezoelectric coefficients; in particular, extraordinarily high values have recently been reported for PZN–PT by Park and Shrout when an electric field is applied along the pseudocubic [001] direction,[1] with $d_{33} > 2500$ pC/N and strain values up to 1.7%. These properties are an order-of-magnitude superior to those of PZT ceramics, currently the materials of choice for a wide variety of high-performance electromechanical devices, and make PZN–PT a promising candidate for the next generation of such devices.[2] In both PZT and PZN–PT, the high-piezoelectric coefficients have been associated with a morphotropic phase boundary (MPB), which separates regions having tetragonal (T) and rhombohedral (R) symmetry. However, the recent discovery of a monoclinic phase in PZT at the MPB has changed this picture dramatically.[3–7] The phase diagrams for the two systems are shown in Fig. 1,[8,9] with the respective MPBs represented as heavy lines and the recently discovered monoclinic structure in PZT (Ref. 3) as M_A. A key feature of this structure is that the polarization vector is no longer constrained to lie along a symmetry axis, as in the rhombohedral and tetragonal structures, but instead can rotate within the monoclinic plane.[4–6]

In the present letter, we report the results of a high-resolution synchrotron x-ray powder diffraction study of a sample doped with 9% PT. This study complements single-crystal investigations of 4.5% and 8% PT samples carried out in collaboration with the Penn State group, which will be reported elsewhere. In particular, measurements made on rhombohedral 8% PT samples under an electric field have shown that an orthorhombic phase is irreversibly induced by the field, indicative of the close proximity of a rhombohedral–orthorhombic boundary in the phase diagram.[10] The presence of some lower-symmetry phase at

room temperature was also revealed in a previous optical study of 9% PT,[11] and the present x-ray results show conclusively the presence of this phase in the PZN–PT phase diagram, which, in contrast to the case of PZT, has orthorhombic rather than monoclinic symmetry.

Compared to the PZT system, PZN–PT has the great advantage that single crystals are relatively easy to grow. A crystal of $Pb(Zn_{1/3}Nb_{2/3})O_3$ containing 9% $PbTiO_3$, identical to those described in Ref. 12, was grown from a PbO flux. It is important to emphasize that in order to obtain sharp powder diffraction peaks from a relaxor-type ferroelectric, it is
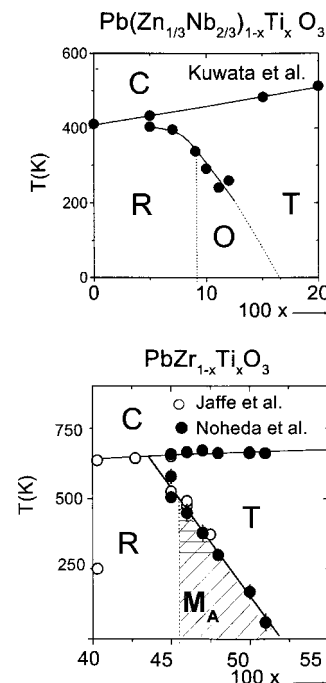
FIG. 1. Phase diagrams for PZT (bottom) and PZN–PT (top) in the vicinity of their respective MPBs (Refs. 8 and 9). *C*, *R*, and *T* represent the cubic, rhombohedral, and tetragonal regions. The diagonally shaded M_A area in the PZT diagram represents the stability region of the recently discovered monoclinic phase (Ref. 7). The proposed stability region in the PZN–PT phase diagram for the orthorhombic phase is labeled *O*.

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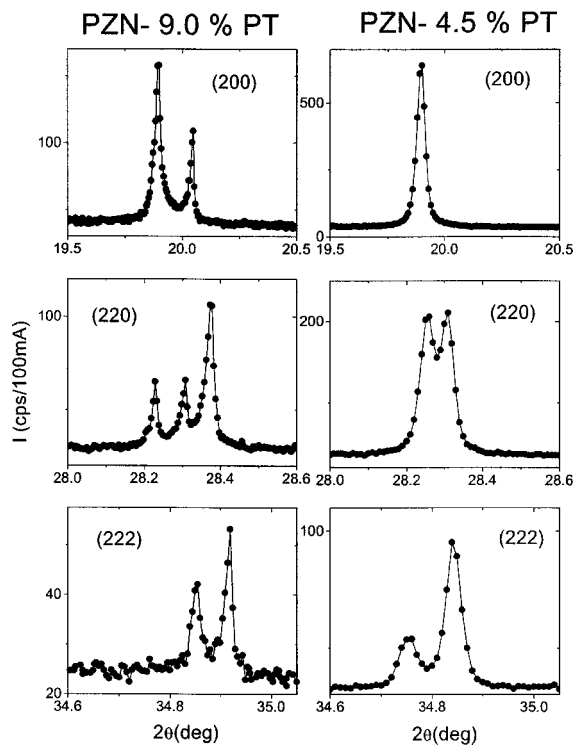FIG. 2. High-resolution synchrotron x-ray diffraction data from polycrystalline samples of PZN containing 9% PT (left) and 4.5% PT (right).
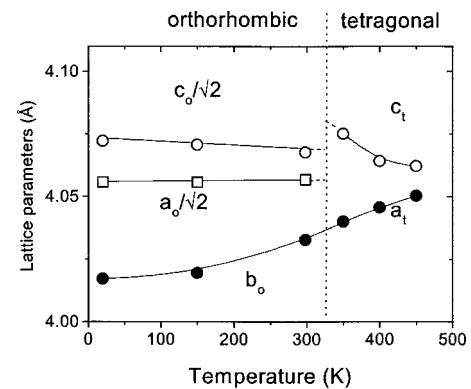

FIG. 3. Variation of orthorhombic lattice parameters for PZN–9% PT as a function of temperature between 20 and 450 K. The sharp discontinuities in a_0 and c_0 with respect to c_t between the orthorhombic and tetragonal regions and the smooth variation of b_0 and a_t are consistent with a jump of the polarization vector from orthorhombic [001] to tetragonal [001], i.e., from pseudocubic [101] to [001].

necessary to induce the ordered ferroelectric state by application of an electric field to the as-grown crystal, and then to give particular attention to the preparation of a suitable polycrystalline sample, since the diffraction peak profiles can be seriously degraded due to the effects of particle size or microstrain broadening caused by excessive grinding. This was accomplished by use of the following procedure. A small fragment was chopped out of the central region of the crystal and lightly crushed and ground in an agate mortar under acetone. The fraction of crystallites retained between 325 and 400 mesh sieves ($\sim 38-44$ μm) was loaded into a thin-walled glass capillary tube 0.2 mm in diameter, which was then sealed. The use of a very-narrow-diameter sample is mandated by the extremely high-absorption coefficients of these materials in the accessible range of wavelengths. High-resolution powder data were collected at the beamline X7A at the Brookhaven National Synchrotron Light Source with a double-crystal Ge(111) monochromator set for a wavelength of ~ 0.7 Å and a flat Ge(220) crystal analyzer mounted in the path of the diffracted beam. The instrumental resolution (full width at half maximum) in this range is $0.005°-0.01°$, an order-of-magnitude better than that of a typical laboratory diffractometer. During data collection, the samples were either rotated at about 1 Hz or rocked over several degrees, which is essential to achieve powder averaging over crystallites of this size. The peaks were found to be extremely sharp and well resolved, as illustrated by the data shown on the left side of Fig. 2. From the splitting and relative intensities of the peaks it is easy to deduce that the sample has neither rhombohedral nor tetragonal symmetry, nor does it consist of a mixture of two such phases in coexistence. However, all the peaks can be indexed very satisfactorily on the basis of a B-centered orthorhombic cell with $a_0 = 5.737$ Å, $b_0 = 4.033$ Å, and $c_0 = 5.759$ Å, similar to that reported for

BaTiO$_3$ in the temperature range 180–270 K.[13] For comparison, similar data obtained from a sample of PZN–4.5% PT are displayed on the right side of Fig. 2. These peaks are somewhat broader but otherwise well resolved; however, in this case the symmetry is unambiguously rhombohedral, as previously reported for this composition,[9] with $a = 4.057$ Å and $\alpha = 89.89°$. The results of the temperature-dependence studies are presented in Fig. 3. Between 350 and 450 K, the symmetry was found to be tetragonal with the c_t/a_t ratio decreasing from 1.009 to 1.003, in agreement with previously reported results.[9] Below room temperature, the system remains orthorhombic down to 20 K, with a steady decrease in b_0 and a small increase in the orthorhombic distortion c_0/a_0 from 1.0027 to 1.0041. In contrast to BaTiO$_3$, there is no further transition to a rhombohedral phase. Although the temperature increments are relatively coarse, the orthorhombic–tetragonal phase transition is clearly first order, as reflected by a sharp discontinuity in the behavior of the a_0 and c_0 lattice parameters. Interestingly, though, there is no such discontinuity between b_0 and a_t, which are perpendicular to the respective polar axes. This behavior is consistent with a first-order transition in which the polar axis jumps from pseudocubic [101] to [001].

In a previous investigation, the diffraction profiles from unpoled single crystals of PZN–9% PT were interpreted in terms of the coexistence of R and T phases.[14] However, a recent analysis of the old data is in complete agreement with the orthorhombic phase. As noted above, this B-centered orthorhombic unit cell is similar to that induced by an electric field in rhombohedral 8% PT.[10] As discussed in the latter paper, it can also be described in terms of a primitive monoclinic cell, space group Pm, with $a = c = 4.062$ Å, $b = 4.033$ Å, and $\beta = 90.15°$. Thus, although we find no evidence of a truly monoclinic distortion (since $a = c$ within the experimental error limits of ~ 0.002 Å), the orthorhombic phase can be regarded as a Pm monoclinic phase (M_C in the notation of Ref. 15) in the limit of $a = c$. However, this is not the same type of monoclinic distortion (M_A in this notation) found in the PZT system,[3,4] which has Cm symmetry.

It is of great interest to view the above results in the light of the recent paper by Vanderbilt and Cohen,[15] hereafter referred to as VC, in which an extension of the Devonshire

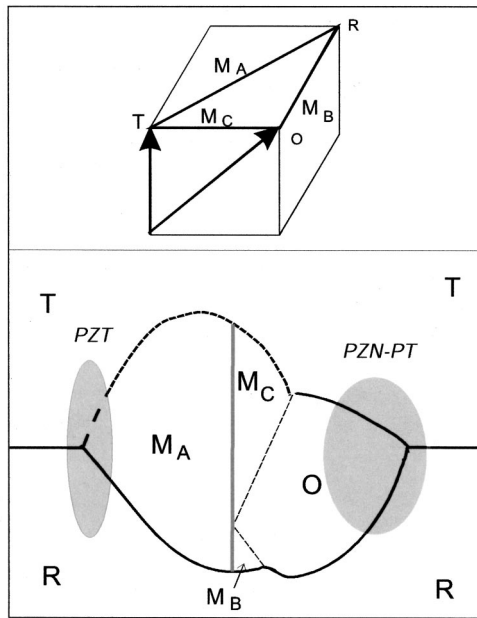Vanderbilt & Cohen phase diagram for ferroelectric perovskites

FIG. 4. Phase diagram for ferroelectric perovskites in the space of the dimensionless parameters α (vertical axis) and β (horizontal axis), which reflect the relative importance of the coefficients of the fourth-, sixth-, and eighth-order terms in the free-energy expansion [after Vanderbilt and Cohen (Ref. 15)]. In the top part of the figure, the T, O, and R phases are depicted as points at the corners of a cube for which the polarization vector (shown by the heavy arrows for T and O) is constrained to lie along a symmetry axis, and the M_A, M_B, and M_C phases as symmetry lines for which the polarization vector lies within a symmetry plane.

theory[16] to eighth order is found to provide a natural description of the recently discovered monoclinic phase in the PZT system.[3,4] The theory also predicts the existence of stability regions for two other types of monoclinic phases and the nature of the boundaries between the various phases. In Fig. 4 we reproduce a slightly modified version of the VC phase diagram in the space of two dimensionless parameters, α and β, which contains stability regions for three kinds of monoclinic phases, labeled M_A, M_B, and M_C, in addition to the T, R, and O phases found in the sixth-order theory. The monoclinic phase in the PZT system is of M_A type (space group Cm). As noted by VC, although α and β cannot be related to temperature or composition in any simple way, it is clear from the data shown in the lower part of Fig. 1 that the MPB in PZT must lie close to the triple-point connecting the R, M_A, and T phases. The PZN–PT system evidently behaves in a quite different fashion. In this case, the discovery of the phase at 9% PT shows that there must be a narrow orthorhombic region the vicinity of the MPB, as shown schematically in the upper part of Fig. 1. Then, it is very plausible that the MPB must lie close to the triple point on the right-hand side connecting the R, O, and T phases, and that 9% PT must fall to the left of this triple point. As can be seen in Fig. 1, the only difference between the two phase diagrams is the structure of the intermediate phase between R and T. As discussed by VC, the clear signature from monoclinic M_A places the PZT system on the phase diagram in the region shown by the shaded area on the left side of Fig. 4. However, the observed orthorhombic phase in PZN–PT does

not uniquely locate the system on this diagram, and our present conjecture is shown by the shaded region on the right side of Fig. 4. We emphasize that so far we have only studied the one composition with 9% PT, and it is possible that compositions between 10% and 12% PT might show the monoclinic M_C structure, which would establish orthorhombic 9% PT as the end member of this monoclinic system.

So far, we have not addressed the important issue of the polarization path under an applied electric field, a topic treated theoretically by Fu and Cohen[17] by applying first-principles calculations to $BaTiO_3$. An experiment of this type carried out on PZN–9% PT may shed light on the question as to whether this orthorhombic phase in this material is fundamentally different from the old orthorhombic phase in $BaTiO_3$. We also anticipate that further insight will be obtained from theoretical calculations of the stability of the $E = 0$ phase, which were so useful in the case of PZT.[6]

In conclusion, we propose that the appearance of a lower-symmetry phase in the vicinity of a MPB over a narrow range of composition and temperature, together with a near-vertical boundary between the lower-symmetry and rhombohedral phases, are universal features of highly piezoelectric perovskite systems. This has important implications for further improving the performance of electromechanical devices since it is just at the MPB that the piezoelectric response is greatly enhanced in PZT and PZN–PT systems. We hope that this will stimulate further work to synthesize systems with MPBs and explore other regions of the phase diagram in Fig. 4.

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