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LETTER TO THE EDITOR

Temperature-induced phase transitions in the giant-piezoelectric-effect material PZN–4.5%PT

J S Forrester[1], **R O Piltz**[2], **E H Kisi**[1] **and G J McIntyre**[3]

[1] Department of Mechanical Engineering, The University of Newcastle, NSW 2308, Australia
[2] Neutron Scattering Section, Australian Nuclear Science and Technology Organisation, PMB 1, Menai NSW 2234, Australia
[3] Diffraction Group, The Institut Laue–Langevin, BP156, Grenoble 38042 Cédex, France

E-mail: jforrest@mail.newcastle.edu.au (J S Forrester), rop@ansto.gov.au (R O Piltz), meehk@cc.newcastle.edu.au (E H Kisi) and mcintyre@ill.fr (G J McIntyre)

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Abstract
Lead zinc niobate–lead titanate (PZN–PT) single crystals are able to sustain very large piezoelectric strains, a phenomenon for which the term ‘giant piezoelectric effect’ was recently coined. PZN–4.5%PT crystals were studied by means of single-crystal neutron diffraction at temperatures between 293 K and 438 K. Two phase transitions were observed. The first, from the room temperature rhombohedral perovskite structure ($R3m$) to the tetragonal lead titanate phase ($P4mm$) occurs at 391 ± 2 K. The second, to the cubic perovskite aristotype, occurs at 421 ± 2 K. These temperatures are at slight variance with the current phase diagram. The transitions are relatively abrupt, occurring over a range of only 2–3 K. A monoclinic phase recently reported to occur between the rhombohedral and tetragonal phases in the lead zirconate titanate system (PZT) does not occur here. Group theoretical analysis using the computer program ISOTROPY indicates that the intermediate monoclinic phase cannot facilitate a truly continuous transition from rhombohedral to tetragonal symmetry.

1. Introduction

Piezoelectric ceramics are widely used for the interconversion of electrical and mechanical energy in a variety of industrial, military and domestic applications [1]. In the design of smart structures and large response actuators, there is considerable demand for piezoelectric materials with large maximum strains.

Recently, single-crystal relaxor ferroelectrics with very large piezoelectric strains have been developed in the lead zinc niobate–lead titanate (PZN–PT) system, at lead titanate (PT) concentrations between 4 and 9% [2, 3]. These concentrations lie close to a morphotropic phase boundary (MPB) on the currently accepted phase diagram [4], in common with the popular lead zirconate titanate (PZT) polycrystalline piezoceramics. PZN–PT crystals in this composition range are reportedly rhombohedral at room temperature and zero applied field [2, 3]. The crystals exhibit maximum piezoelectric strains up to 1.7% at electric fields up to 130 kV cm^{-1}, a property for which the term 'giant piezoelectric effect' was recently coined [5].

Several features of this behaviour are poorly understood including:

(i) why the maximum piezoelectric strain is directed along [001] and not the spontaneous polarization direction of the crystals [111],
(ii) how the crystals survive such large strains without fracturing and
(iii) the mechanism by which the effect operates.

Various mechanisms for the large piezoelectric strains have been postulated. First it was noted that the high-field piezoelectric and dielectric constants are the same as those of the tetragonal phase, suggesting that the material undergoes a rhombohedral-to-tetragonal phase transition under an applied electric field [3, 6, 7]. Such a transition is necessarily first order. Other groups have suggested that the effect is merely the result of very large elastic compliance along [001] [4]. Next, it was postulated that the crystals can survive the transition because of an engineered domain structure where four of the eight possible rhombohedral $\langle 111 \rangle$ domains in a [001]-oriented crystal are chosen by a careful electric poling procedure [8]. Most recently, the possibility of a continuous polarization rotation under applied field has been shown using lattice statics calculations [5]. This latter behaviour is necessarily second order and implies that the sequence of phases postulated in the earlier work is not correct.

It has been demonstrated [4, 9] that the piezoelectric properties of PZN–PT are closely correlated with the MPB. This is also the case for PZT ceramics, although the maximum piezoelectric coefficient occurs just before the MPB in the former and within the MPB in the latter. The precise nature of MPBs, e.g. whether they are first order or second order, has been the subject of considerable debate, particularly in the technologically important PZT system. A first-order boundary implies the existence of a two-phase region and this has been reported many times in the literature [10–14]. Proponents of a second-order boundary [15, 16] have suggested that the two-phase region results from chemical inhomogeneity imposed by lead loss during firing. Because the phase relationships around the MPB in PZN–PT are very similar to those in PZT, similar uncertainties exist. Polarizing microscopy results obtained using PZN–9%PT single crystals suggest that the MPB in PZN–PT is a mixture of the rhombohedral and tetragonal phases implying a first-order boundary [17, 18]. Likewise, the electric property measurements of Kuwata *et al* [4] indicate a first-order MPB.

Recently, Noheda *et al* discovered a monoclinic intermediate phase at the MPB in PZT [19–21]. This new phase was observed using synchrotron x-ray powder diffraction and a structure was refined in the space group Cm. Initially, the monoclinic phase was proposed, on the basis of group–subgroup relationships, to facilitate a continuous transition from rhombohedral to tetragonal symmetry across the boundary [20]. A more comprehensive survey of the composition–temperature phase diagram has shown that the monoclinic phase exists in a wedge-shaped region within what was formerly the rhombohedral phase field, adjacent to the MPB [21]. A region of rhombohedral/tetragonal boundary persists at lower Ti compositions. Additionally, it was found that the monoclinic phase exists over a wider range of composition under an applied electric field than in zero field. The tetragonal-to-cubic transition was found to be continuous whereas the monoclinic-to-tetragonal and rhombohedral-to-tetragonal transitions were observed to be first order. The boundary between the rhombohedral and monoclinic phases is nearly vertical and no results concerning the order of this transition were reported.

The same group has now proposed that a similar though distinct monoclinic phase exists in the PZN–PT system close to the MPB, based upon *in situ* high-energy x-ray diffraction of an 8%PT single crystal under the action of an imposed electric field [22]. The unpoled crystal used in their work showed a rhombohedral-to-monoclinic transition in lattice parameter data recorded with increasing electric field applied along the [001] direction, and remained monoclinic upon removal of the field. At higher field values, the monoclinic phase appeared to be approaching a further transition to a tetragonal phase. As the maximum field used in those experiments, 20 kV cm^{-1}, is much less than that required for the maximum piezoelectric strains ($\sim$130 kV cm^{-1}) the high-field behaviour remains unknown. Noheda *et al* [22] anticipate, from the analogy with the PZT system, that the temperature–composition phase diagram will also show the monoclinic phase, at around 8%PT, although the temperature evolution of the structure was not studied by those authors.

As part of a comprehensive *in situ* neutron diffraction study of the phase evolution in both temperature and electric field, we present here the results for PZN–4.5% PT crystals studied by means of high-resolution single-crystal neutron diffraction in the range 293–438 K.

2. Group theoretical analysis

Recent work by Howard, Stokes and others [23–25] has shown the power of group theoretical analyses in perovskites beset with pseudo-symmetries that can confound even the highest-resolution diffraction instruments. Such analyses are greatly simplified by the use of the computer program ISOTROPY [23]. By examining all isotropy subgroups of the perovskite aristotype $Pm\bar{3}m$ that have, as the primary order parameter, a ferroelectric displacement of the B cation within the oxygen octahedra, the diagram in figure 1 can be constructed. Transitions that may be second order are shown by solid lines and those that must be first order are shown dashed. It can be seen from this analysis that, as expected, no second-order transition is allowed between the rhombohedral ($R3m$) and tetragonal ($P4mm$) phases of PZN–PT. The analysis also indicates that whilst Cm is a subgroup of $R3m$, the transition cannot be second order because it allows a cubic invariant and violates the Landau condition. There is no

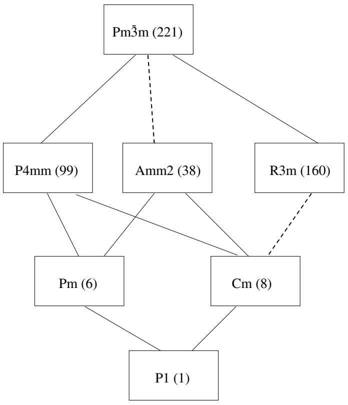

Figure 1. Space groups generated in the program ISOTROPY, by allowing a ferroelectric distortion of the cubic aristotype structure by displacement of the B cation within the anion octahedra. Lines between space groups indicate a group–subgroup relationship. Solid lines indicate that the transition is allowed to be second order whereas transitions represented by dashed lines must be first order.

group–subgroup relationship between $R3m$ and the other monoclinic space group in figure 1, Pm. The analysis presented thus far has ignored the influence of octahedral tilting. A similar analysis can be conducted where the ferroelectric distortion is coupled with the tilt patterns identified by Howard and Stokes [24]. This analysis shows that there is likewise no credible second-order transition between the rhombohedral and monoclinic symmetries.

3. Experimental procedure

PZN–4.5%PT crystals 2 × 2 × 2 mm were purchased from TRS Ceramics (Suite J, 2820 East College Avenue, State College, PA 16801). The composition chosen exhibits the giant piezoelectric effect and although it does not have the highest piezoelectric strain, has the advantage of being well clear of the MPB at room temperature and of meeting the MPB at a far less acute angle on the current phase diagram than the other popular compositions 8% and 9% PT. In this work, pre-poled [111]-oriented crystals were used to ensure that the starting crystals were single domain. Room temperature measurements were conducted on the instrument 2TANA, a conventional four-circle instrument with a peak resolution of approximately 0.25° 2θ, at the Australian Nuclear Science and Technology Organisation (ANSTO) HIFAR reactor. The phase transitions were studied on an ultralow-background four-circle instrument fitted with an area detector, D10 at the Institut Laue–Langevin (ILL), Grenoble, France. The D10 sample was mounted in a cryo-furnace with the temperature controlled to within 0.1 K and calibrated to within 2 K.

Data were recorded using an incident wavelength of 1.26 Å with less than 10^{-4} $\lambda/2$ contamination, a feature particularly useful in checking for superlattice reflections and diffuse scattering. The data collection strategy included a full data set (513 reflections) at 295 K, a subset of 29 reflections at 10 K intervals in the range 353–383 K, a set of 11 reflections at 1 K intervals in the range 388–438 K with every fifth set being 29 reflections. Data were also collected at 1 K intervals during cooling from 438 to 393 K. Zone scans, superlattice scans and diffuse scans were also conducted.

Unit-cell data were analysed using ILL software and programs developed at ANSTO. Peak centres were initially determined by RACER followed by cell refinements using RAFD9. A new cell refinement program, UBREF, that compensates for non-centring of the crystal in the diffractometer goniometer was used in the latter stages of the analysis. The unit-cell refinements were corrected for sample positioning errors by refining a set of crystal offsets in the cubic region and then applying these offsets at all temperatures. Thermal expansion was found to have negligible effect on this correction and the resulting lattice parameters. The crystals are pseudo-cubic and so cells were initially refined unconstrained (i.e. as triclinic). Later cell refinements were constrained to have the symmetry indicated by the unconstrained refinements. At temperatures close to the phase transitions, both possible symmetries were refined and compared on the basis of the mean square deviation of calculated and observed diffractometer angles. Orthorhombic and monoclinic cells were also tested without improvement of the fits. Integrated intensities and FWHM were extracted from the data using the ILL computer program RACER and a commercial peak-fitting program, PEAKFIT.

4. Results and discussion

In all of what follows, it should be understood that this system exhibits severe pseudo-symmetry. All of the unit cells are pseudo-cubic to within $<0.1\%$. Unconstrained unit-cell refinements indicated that the room temperature structure is rhombohedral, in agreement with previous work [2, 3]. Data acquisition at all $h \pm \frac{1}{2}$, $k \pm \frac{1}{2}$, $l \pm \frac{1}{2}$ superlattice positions found no intensity above background, confirming that the room temperature space group is $R3m$. Testing of various monoclinic cells did not lead to an improved agreement with the data. Zone scans along various reciprocal-space directions failed to find evidence of diffuse scattering between the Bragg peaks, indicating that the crystals are well ordered. Preliminary intensity calculations indicate severe primary extinction, resulting from the high degree of crystal perfection.

4.1. Transition temperatures and symmetry

Unconstrained (triclinic) unit-cell refinements gave the results shown in figure 2(a). A phase transition resulting in orthogonalization of the unit cell and splitting of the axial lengths can be observed at 390 ± 5 K. The rotation of the cell angles is shown more clearly in figure 2(b), from refinements conducted on the assumption of rhombohedral symmetry over the whole range of temperature. A second transition in which the cell dimensions return to being equal (i.e. cubic) occurs at 419 ± 5 K.

Although the unconstrained cell refinements in figure 2(a) suggest that the symmetry above 390 K is orthorhombic, the best refined unit cell for this phase is tetragonal with $a > c$. However, as the tetragonal phase is known to be ferroelectric [4], it is expected to have $a < c$. This apparent reversal can be explained by the typical striped domain structure found in tetragonal ferroelectrics. This domain structure has domain walls along (101) planes with adjacent domains appearing to be 90° rotations of each other about the b-axis. The pseudo-cubic unit cell prevents the resolution of the overlapping reflections from different 90° domains, resulting in a refined unit cell that represents an average of the two domain types. Within the temperature range 401 to 411 K, the refined unit cell has $a = c = 4.0612$ Å and $b = 4.0563$ Å which, if interpreted as the average of two 90° domains, gives the true cell dimensions as $a = b = 4.0563$ Å and $c = 4.0661$ Å. The pseudo-symmetry is so severe that the overlapping domains cause only minor broadening of the highest-symmetry reflections (e.g. {200}). An analysis of the reflection broadening for other (hkl) supports the above conclusions.

Both transitions are more clearly seen in figure 2(c) where the results of symmetry-constrained unit-cell refinements are shown. Unit-cell dimensions are given for a rhombohedral cell at $\leqslant$393 K, a tetragonal cell between 393 and 419 K and a cubic cell thereafter. Close to the transitions, refinement results are shown for both potential symmetries.

Ample further evidence for the transitions is found in the integrated intensities and peak widths. Some examples are shown in figure 3 for a strong, (200), and a weak, (211), reflection. All of the reflections showed transitions at the same temperatures. The transitions are far more distinct in figure 3 than in figure 2 and allow us to refine the transition temperatures to 391 ± 2 K and 421 ± 2 K respectively. These temperatures are lower than on the current phase diagram [4] (413 and 433 K) and the tetragonal phase in our crystals persists over a wider temperature range. The transitions appear to be relatively abrupt with ΔT being only 2–3 K. The intensity changes observed are primarily due to changes in the crystal mosaic and the associated primary extinction. The starting crystal, poled along the direction of spontaneous polarization, suffers considerable extinction and is therefore assumed to be relatively perfect. As the crystal transforms into the tetragonal phase via a first-order transition, a new domain structure is established which reduces extinction and the intensities in figure 3 increase markedly. The partitioning of the crystal into domains, and the associated lattice mismatch, is also apparent from the increased FWHM of the reflections in figure 3. In undergoing the second transition to cubic, the symmetry is raised, adjacent domains become equivalent and amalgamate to form a more perfect crystal, and so the extinction returns. This interpretation is confirmed by the observation that the strong reflections show a much greater proportional change in intensity

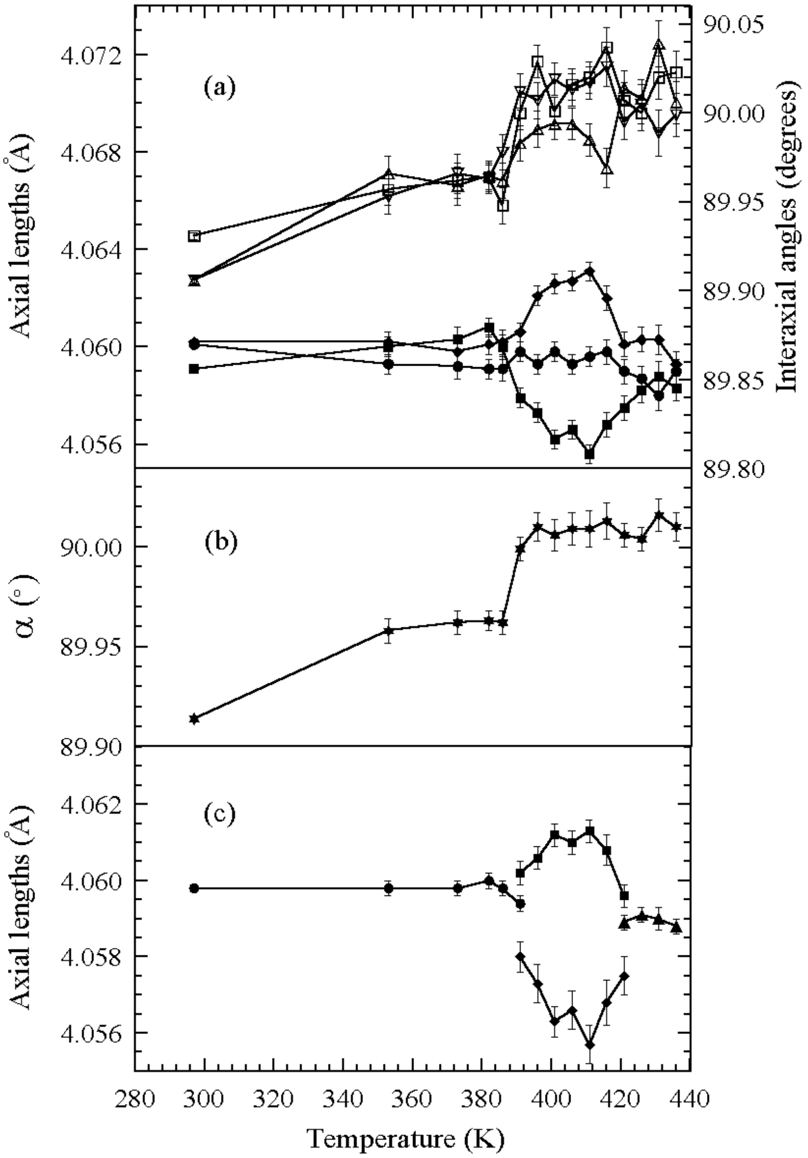

Figure 2. Lattice parameters for a PZN–4.5%PT crystal heated to 438 K refined as (a) triclinic, (b) rhombohedral and (c) rhombohedral, tetragonal or cubic depending on the temperature. In part (a), the axial lengths are given by solid symbols and the interaxial angles open symbols.

than the weak reflections. The intensity and FWHM of the tetragonal peaks are not constant, but steadily move in the direction of a more perfect crystal as the temperature increases. This may be due to domain growth driven by the approach of a continuous transition to the cubic phase or by a process similar to annealing with time.

In our experiments, the shortest neutron diffraction data collections (11 reflections) took 30 minutes whereas the longer data collections (29 reflections) took of order 90 minutes. Careful scrutiny of the data collected during heating reveals a very small though systematic difference in increasing sample perfection for a short data collection and a longer one. This

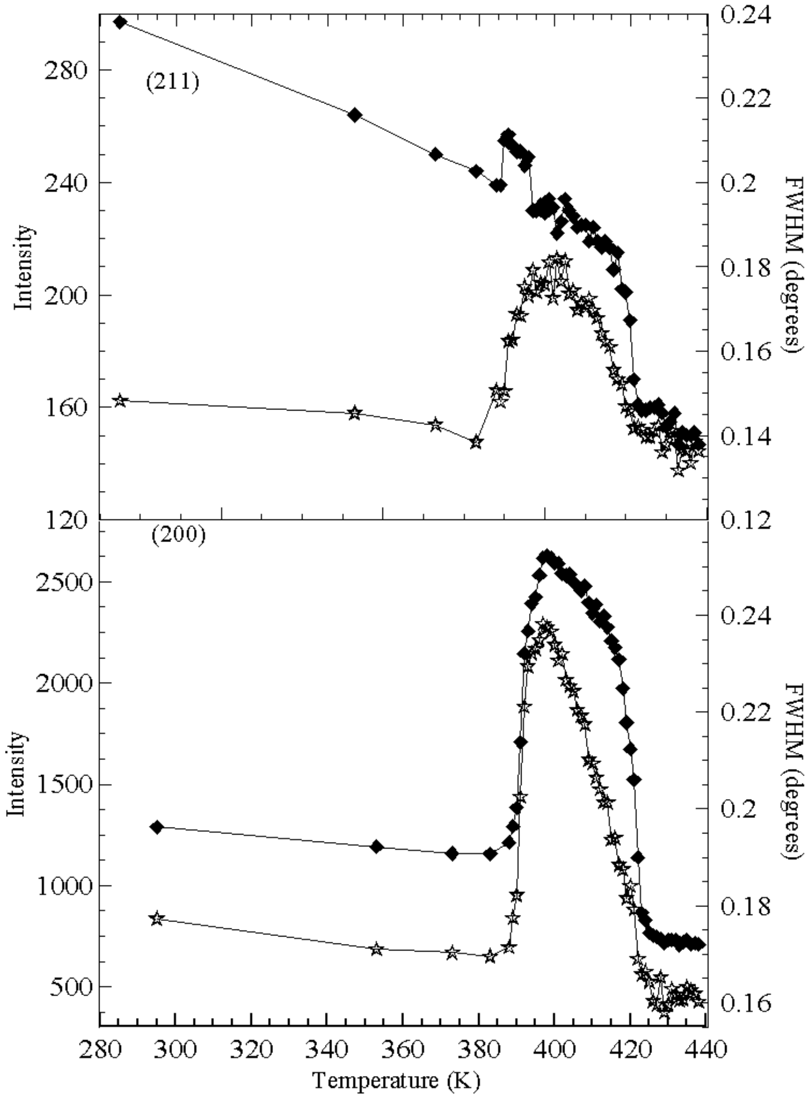

Figure 3. Integrated intensity (solid symbols) and peak full width at half-maximum height FWHM (open symbols) for a weak (211) and strong (200) reflection.

observation suggests that domain growth mainly occurs due to the increase in temperature not time i.e. it is driven by the approaching transition. On cooling, there appears to be temperature hysteresis in the transition temperatures and the transition is spread over a wider temperature range than on heating. As these crystals are somewhat removed from the MPB and hence harder ferroelectrics compared with MPB compositions, we believe that the observed hysteresis is due to kinetic factors associated with the establishment of a domain structure in the tetragonal phase.

4.2. The monoclinic phase [22] and the PZN–PT phase diagram

Our results appear to contradict the prediction of Noheda *et al* [22] that the MPB in the PZN–PT system is necessarily associated with a monoclinic phase as no such phase was observed in our data. Two alternative possibilities must be considered. First, there is the possibility that a rhombohedral-to-monoclinic transition occurs below 391 K. This is ruled out by the intensity and FWHM data (e.g. see figure 3) where there is clearly no transition in the range 293–391 K. Second, there is the possibility that our tetragonal phase is a tetragonal-like admixture of monoclinic domains over some of its temperature range. Whilst we cannot rule it out completely, this possibility is considered unlikely because the data were collected using an area detector. Monoclinic lattice parameters such as those found by Noheda *et al* would split reflections like the {200} group by up to 0.3 degrees—easily resolvable in our experiment. No such splitting was observed. Our crystal appears to have undergone only two transitions, a first-order rhombohedral-to-tetragonal and a (most probably) second-order tetragonal-to-cubic transition. This means that:

(i) the monoclinic phase exists over a narrow composition range that does not extend to compositions as low as 4.5%PT, or

(ii) in the PZN–PT system, a monoclinic phase only appears under an applied electric field.

By analogy with recent results in the PZT system [21] our crystals are likely to lie *outside* the zero-field range of the monoclinic phase and, because these 4.5%PT crystals also show the giant piezoelectric effect, *inside* the range where the monoclinic phase can be induced by an electric field. The precise relationship between the temperature- and field-induced phases remains to be established.

In an earlier section it was highlighted, on group theoretical grounds, that the monoclinic phase cannot facilitate a strictly continuous rotation from rhombohedral to tetragonal symmetry. However, as has been highlighted by Noheda *et al* [21], the monoclinic structure has a great degree of freedom in the direction of the polarization vector, which may allow it to nonetheless serve as an effective intermediate structure.

Lastly, these new results allow us to comment on the phase diagram. The current diagram, redrawn from Kuwata *et al* [4], is shown in figure 4. Our transition temperatures are shown as solid points and suggest that the transition temperatures on the diagram need to be modified by a downward shift. The consequences of these changes are fairly minor; however, they do

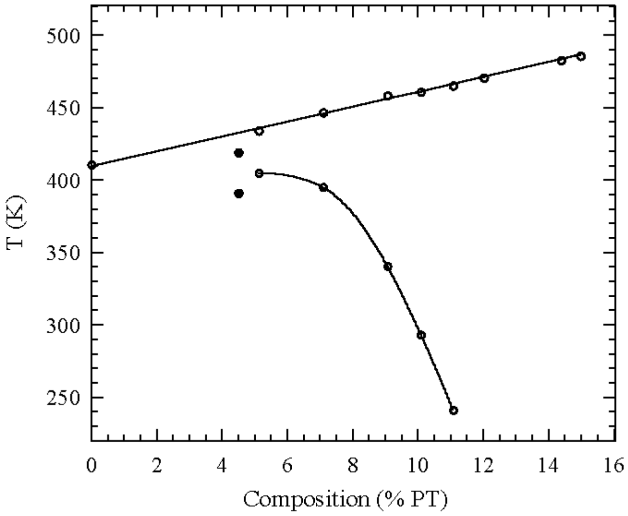

Figure 4. The PZN–PT phase diagram with the transition temperatures determined in this work shown as solid symbols.

indicate that the maximum operating temperatures of these crystals, when used in piezoelectric applications, is lower than previously thought.

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References

[1] Newnham R E and Ruschau G R 1991 *J. Am. Ceram. Soc.* **74** 463–80
[2] Service R F 1997 *Science* **275** 1878
[3] Paik D-S, Park S-E, Wada S, Liu S-F and Shrout T R 1999 *J. Appl. Phys.* **85** 1080–3
[4] Kuwata J, Uchino K and Nomura S 1981 *Ferroelectrics* **37** 579–82
[5] Fu H and Cohen R E 2000 *Nature* **403** 281–3
[6] Park S-E and Shrout T R 1997 *J. Appl. Phys.* **82** 1804–11
[7] Durbin M K, Jacobs E W, Hicks J C and Park S-E 1999 *Appl. Phys. Lett.* **74** 2848–50
[8] Wada S, Park S-E, Cross L E and Shrout T R 1999 *Ferroelectrics* **221** 147–55
[9] Park S-E, Vedula V, Pan M-J, Hackenberger W S, Pertsch P and Shrout T R 1998 *Proc. SPIE—Int. Opt. Eng.* **3324** 136–44
[10] Ari-Gur P and Benguigui L 1975 *J. Phys. D: Appl. Phys.* **8** 1856–62
[11] Isupov V A 1975 *Solid State Commun.* **17** 1331–3
[12] Singh A P, Mishra S K, Lal R and Pandey D 1995 *Ferroelectrics* **163** 103–13
[13] Mishra S K, Singh A P and Pandey D 1997 *Phil. Mag.* B **76** 213–26
[14] Soares M R, Senos A M R and Mantas P Q 1999 *J. Eur. Ceram. Soc.* **19** 1865–71
[15] Kakegawa K, Mohri J, Shirashki S and Takehashi K 1982 *J. Am. Ceram. Soc.* **65** 515–19
[16] Lal R, Krishnan R and Ramakrishnan P 1988 *Br. Ceram. Trans. J.* **87** 99–102
[17] Ye Z G, Dong M and Zhang L 1999 *Ferroelectrics* **229** 223–32
[18] Fujishiro K, Vlokh R, Uesu Y, Yamada Y, Kiat J-M, Dkhil B and Yamashita Y 1998 *Japan. J. Appl. Phys.* **37** 5246–8
[19] Noheda B, Cox D E, Shirane G, Gonzalo J A, Cross L E and Park S-E 1999 *Appl. Phys. Lett.* **74** 2059–61
[20] Noheda B, Gonzalo J A, Cross L E, Guo R, Park S-E, Cox D E and Shirane G 1999 *Phys. Rev.* B **61** 8687–95
[21] Noheda B, Cox D E, Shirane G, Guo R, Jones B and Cross L E 2000 *Phys. Rev.* B **63** 14 103
[22] Noheda B, Cox D E, Shirane G, Park S-E, Cross L E and Zhong Z 2001 *Phys. Rev. Lett.* **86** 3891–4
[23] Stokes H T *'ISOTROPY'* www.physics.byu.edu/~stokesh/isotropy.html
[24] Howard C J and Stokes H T 1998 *Acta Crystallogr.* B **54** 782–9
[25] Howard C J, Knight K S, Kennedy B J and Kisi E H 2000 *J. Phys.: Condens. Matter* **12** L677–83