Elastic and anelastic relaxation behaviour of perovskite multiferroics I: PbZr\(_{0.53}\)Ti\(_{0.47}\)O\(_3\) (PZT)–PbFe\(_{0.5}\)Nb\(_{0.5}\)O\(_3\) (PFN)

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ABSTRACT

Perovskites in the ternary system PbTiO\(_3\) (PT)–PbZrO\(_3\) (PZ)–Pb(Fe\(_{0.5}\)Nb\(_{0.5}\))O\(_3\) (PFN) have attracted close interest because they can display simultaneous ferroelectric, magnetic and ferroelastic properties. Those with the most sensitive response to external fields are likely to have compositions near the morphotropic phase boundary (MPB) which lies close to the binary join Pb(Zr\(_{0.53}\)Ti\(_{0.47}\))O\(_3\) (PZT)–PFN. In the present study, the strength and dynamics of strain coupling behaviour which accompanies the development of ferroelectricity and (anti)ferromagnetism in ceramic PZT–PFN samples have been investigated by resonant ultrasound spectroscopy. Elastic softening ahead of the cubic–tetragonal transition does not fit with models based on dispersion of the soft mode or relaxor characteristics but is attributed, instead, to coupling between acoustic modes and a central peak mode from correlated relaxations and/or microstructure dynamics. Softening of the shear modulus through the transition by up to ~50 % fits with the expected pattern for linear/quadratic strain/order parameter coupling at an improper ferroelastic transition and close to tricritical evolution for the order parameter. Superattenuation of acoustic resonances in a temperature interval of ~100 K below the transition point is indicative of mobile ferroelastic twin walls. By way of contrast, the first-order tetragonal–monoclinic transition involves only a small change in the shear modulus and is not accompanied by significant changes in acoustic dissipation. The dominant

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feature of the elastic and anelastic properties at low temperatures is a concave-up variation of the shear modulus and relatively high loss down to the lowest temperature, which appears to be the signature of materials with substantial local strain heterogeneity and a spectrum of strain relaxation times. No evidence of magnetoelastic coupling has been found, in spite of the samples displaying ferromagnetism below ~550 K and possible spin glass ordering below ~50 K. For the important multiferroic perovskite ceramics with compositions close to the MPB of ternary PT-PZ-PFN, there must be some focus in future on the role of strain heterogeneity.

Introduction

A characteristic approach for tailoring desirable properties of materials for device applications is to make use of solid solutions. This is achievable in the case of multiferroic perovskites, for example, by combining the ferroelectric properties of Pb(Zr,Ti)O₃ (PZT) with the ferro/antiferromagnetic properties of Pb(Fe₀.₅Nb₀.₅)O₃ (PFN) or Pb(Fe₀.₅Ta₀.₅)O₃ (PFT) [1–6], producing a successful demonstration of magnetic switching of ferroelectric domains at room temperature in single crystals with nominal composition \[\text{Pb(Zr}_{0.₃} \text{Ti}_{0.₇})\text{O}_₃\]₀.₆\[\text{Pb(Fe}_{0.₅} \text{Ta}_{0.₅})\text{O}_₃\]₀.₄ [7–9]. The same approach has been successful also in the development of magnetoelectric thin films with compositions between \[\text{Pb(Fe}_{0.₆} \text{W}_{0.₄})\text{O}_₃\] and \[\text{Pb(Zr}_{0.₅} \text{Ti}_{0.₄})\text{O}_₃\] [10, 11]. In other magnetoelectric perovskites, the ferroelectricity often arises from Pb or Bi at the A-site and magnetism from Fe or Mn at the B-site, but in PZT–PFN and PZT–PFT, the ferromagnetism and the ferroelectricity both arise from the same ion (Fe³⁺) at the B-site [12]. This leads to an unusually high magnetoelectric coupling and a high-temperature multiferroic state.

An important coupling mechanism between magnetic and electric dipoles in PZT–PFT could be by strain mediation [7]. Applying the magnetic field induces a change in magnetic moments, and a strain due to magnetoelastic coupling would then cause a change in the ferroelectric moment, or vice versa, with the implication that the elastic strain relaxations might be as important as the primary ferroic properties. The ferroelectric transition(s) involve changes in symmetry from cubic to tetragonal, rhombohedral or monoclinic so that they are also ferroelastic, which means that the dielectric properties are necessarily coupled with shear strain. Much less is known about strain coupling with the ferromagnetic and/or antiferromagnetic order parameters.

The purpose of the present study was to characterise the overall strain relaxation behaviour of selected members of the PZT–PFN and PZT–PFT solid solutions by experimental determination of elastic and anelastic properties. Variations of the shear modulus provide a highly sensitive measure of the strength of intrinsic strain coupling effects associated with phase transitions, while acoustic losses are indicative of dynamical relaxation behaviour of defects such as twin walls or the boundaries between polar nano regions. In part I (this paper), we report results for \[\text{Pb(Zr}_{0.₃} \text{Ti}_{0.₇})\text{O}_₃\]–PFN, and in part II [13], we report results for \[\text{Pb(Zr}_{0.₃} \text{Ti}_{0.₄})\text{O}_₃\]–PFT.

Phase transitions and location of the morphotropic phase boundary within the PT-PZ-PFN ternary system

Following the long established understanding of PZT, the expectation is that the largest variations in dielectric properties for PZT–PFN solid solutions could occur in the vicinity of the MPB, hence the focus on compositions close to this within the ternary system PbTiO₃ (PT)–PbZrO₃ (PZ)–PFN. Structural relationships in the ternary system have not been fully investigated, but their form can be sketched out from the known behaviour of the three binaries and a limited number of experimental results for ternary compositions.

PT-PFN

PT has a cubic (Pm̅3m)–tetragonal (ferroelectric, P4mm) transition at ~760 K which is weakly first
order but close to a tricritical point [14–19]. The same transition extends along the PT-PFN binary [20]. The sequence of structural transitions with falling temperature in PFN is cubic (Pm\(\overline{3}m\), or Fm\(\overline{3}m\) if there is B-site ordering)–tetragonal (P4\(mm\))–monoclinic (Cm). At least in some samples, the low temperature structure may be rhombohedral (R3m) [21]. The first transition is close to tricritical in character and typically occurs at \(\sim 380–390\) K. The second, 20–40 K lower, is generally considered to be first order in character [21–31]. With increasing PT content along the PFN–PT binary join, the stability field of the monoclinic structure diminishes such that the P4\(mm\)–Cm transition point extrapolates to 0 K at \(\sim 8–12\%\) PT [32, 33].

**PZ–PFN**

PZ has a first-order transition from cubic (paraelectric, Pm\(\overline{3}m\)) to orthorhombic (antiferroelectric, Pbam) at \(\sim 500\) K, sometimes with and sometimes without a small intermediate stability field of a few degrees for the rhombohedral (ferroelectric, R3m) structure [34–37]. The Pbam structure is restricted to low PT and low PFN contents (i.e. near to PZ) [38–42]. It is likely that the cubic (Pm\(\overline{3}m\))–rhombohedral (R3m) transition is close to tricritical since it passes through a tricritical point with increasing PT content along the PT–PFN join [43].

For most of the PZ–PFN solid solution, the ferroelectric structure is rhombohedral [39–41]. Additional transitions between rhombohedral phases at compositions close to the Pbam—rhombohedral phase boundary and near the 50:50 composition have been proposed [40, 41], but the structures involved were not fully characterised. By analogy with the topology of the PZ-rich side of the PZ–PT phase diagram shown by Cordero et al. [44], one possibility is that high temperature and lower temperature ferroelectric phases labelled by Lovkova et al. [41] as FE\(_2\) and FE\(_3\) correspond to R3m and R3c structures, respectively. This would have the R3m–R3c transition temperature increasing from \(\sim 300\) K at 10 % PFN to \(\sim 330\) K at 20 % PFN. Whatmore and Bell [45] appear to have placed the transition at \(\sim 300\) K for 5 % PFN and \(\sim 330\) K for 10 % PFN, but the trend of increasing transition temperature with increasing PFN content is the same.

**Ternary compositions**

The P4\(mm\) structure that extends along most of the PT–PFN join and along the PT–PZ boundary towards the MPB is expected to occur all across the PT-rich side of the MPB in the ternary system. Tetragonal lattice geometry has been confirmed at room temperature for three compositions in the middle of this field [46], at three compositions along the join Pb(Zr\(_{0.44}\)Ti\(_{0.56}\))O\(_3\)-PFN [47] and close to the ternary MPB [48].

The PZ-rich side of the binary MPB in PT–PZ has an additional octahedral tilting transition with a maximum transition temperature of \(\sim 420\) K at \(\sim 15\%\) PT [38]. This phase boundary extrapolates to the location of the MPB at \(\sim 160\) K, \(\sim 50\%\) PT [38, 44, 49], though extrapolation to \(\sim 0\) K at \(\sim 50\%\) PT has also been shown in some phase diagrams [50, 51]. Diffraction and dielectric evidence for a tilting transition at \(\sim 210\) K in Pb(Zr\(_{0.52}\)Ti\(_{0.48}\))O\(_3\) [52, 53] is consistent with the topology given by Cordero et al. [44] and calculated from first principles by Kornev et al. [54]. Away from the MPB, the change in space group is R3m–R3c, for which second-order character is allowed. Data for PbZr\(_{0.9}\)Ti\(_{0.1}\)O\(_3\) appear to show that this transition is weakly first order [55], but it is continuous with varying composition at room temperature [56]. As discussed above, this same transition may also occur along the PZ–PFN binary join and would give a stability field for the R3c structure extending into the ternary system at room temperature. In the stability field of the monoclinic structure below the MPB of PZT, the same octahedral tilting transition involves the symmetry change Cm–Cc [57–62], but no information is yet available to determine whether this occurs in the ternary system as well. In (Pb\(_{0.94}\)Sr\(_{0.06}\))(Zr\(_{0.55}\)Ti\(_{0.45}\))O\(_3\), the Cm–Cc transition is thermodynamically continuous [63].

The stability limit of the Cm structure of PFN within the ternary system is not known but, just as for PZT, is presumed to be closely linked to the position of the MPB. Fang et al. [48] reported that they were expecting to find a rhombohedral structure at compositions on the PZ side of the MPB but that the distortion from cubic lattice geometry was below the limit of resolution of their diffraction data. PFN-rich compositions along the join Pb(Zr\(_{0.44}\)Ti\(_{0.56}\))O\(_3\)-PFN were reported by Amonpattaratkit et al. [47] as
being cubic at room temperature but could presumably have been rhombohedral or monoclinic with only very small lattice distortions. The same applies toPFN-rich compositions along the join Pb(Zr0.53 Ti0.47)O3–PFN, with a two phase mixture (cubic \( \rightarrow \) tetragonal) at 30 % PFN [64].

The location of the room temperature MPB has been determined at three ternary compositions in ceramic samples by Fang et al. [46, 48, 65]. These three compositions, the binary phase diagram for PZT from Jaffe et al. [38] and in PT–PFN from Singh et al. [33], Sitalo et al. [32]. Blue squares tetragonal samples at room temperature [3, 46, 47, 64, 68–70]. Brown squares ternary compositions described as cubic by Amonpattaratkit et al. [47] but which are most likely rhombohedral or monoclinic with small strains. Filled green squares ternary compositions described as cubic by Yu et al. [64] but which are most likely rhombohedral or monoclinic with small strains. Open green square ternary composition described as containing both cubic and tetragonal phases [64]. The sample at \([\text{Pb(Zr}_{0.44}\text{Ti}_{0.56})\text{O}_3]_{0.9} \cdot \text{PFN}_{0.1}\) is shown as tetragonal, based on the reported diffraction pattern [67]. Other boundaries in PT–PZ from Jaffe [38], Cordero et al. [49], PZ–PFN from Lovkova et al. [41] and Blazhievskii et al. [40]. Red crosses mark nominal compositions of samples used in the present study, along the join Pb(Zr0.53 Ti0.47)O3–PFN. The rhombohedral structure type at room temperature for most of the PZ-rich side of the ternary MPB is not known.

Figure 1 Section of the ternary PT–PZ–PFN system at room temperature. Solid bars location of ternary MPB from Fang et al. [48]; solid circles location of MPB in PT–PZ from Jaffe et al. [38], and in PT–PFN from Singh et al. [33], Sitalo et al. [32]. Blue squares tetragonal samples at room temperature [3, 46, 47, 64, 68–70]. Brown squares ternary compositions described as cubic by Amonpattaratkit et al. [47] but which are most likely rhombohedral or monoclinic with small strains. Filled green squares ternary compositions described as cubic by Yu et al. [64] but which are most likely rhombohedral or monoclinic with small strains. Open green square ternary composition described as containing both cubic and tetragonal phases [64]. The sample at \([\text{Pb(Zr}_{0.44}\text{Ti}_{0.56})\text{O}_3]_{0.9} \cdot \text{PFN}_{0.1}\) is shown as tetragonal, based on the reported diffraction pattern [67]. Other boundaries in PT–PZ from Jaffe [38], Cordero et al. [49], PZ–PFN from Lovkova et al. [41] and Blazhievskii et al. [40]. Red crosses mark nominal compositions of samples used in the present study, along the join Pb(Zr0.53 Ti0.47)O3–PFN. The rhombohedral structure type at room temperature for most of the PZ-rich side of the ternary MPB is not known.
Pb(Zr0.53Ti0.47)O3-PFN

The topology of Fig. 1 shows that end member PFN itself and samples used in the present study along the binary join between Pb(Zr0.53Ti0.47)O3 and PFN are all close to the MPB. It is consistent with tetragonal structures reported by Kumar et al. [70] at 50 % PFN and by Sanchez et al. [3] for four compositions with 10, 20, 30 and 40 % PFN. Known structural transitions along this join are shown in Fig. 2. Based on the phase diagrams of Jaffe et al. [38] and Cordero et al. [44], the expectation for Pb(Zr0.53Ti0.47)O3 is $Pm3m$ – $P4mm$ – $Cm$ – $Cc$, with transitions at $\sim 650$, $\sim 315$ and $\sim 190$ K which are permitted by symmetry to be thermodynamically continuous. The temperatures of a peak in the dielectric constant, $T_m$, at three compositions along the binary join [48] and at one composition close to it [70] fall along a linear trend between the transition temperatures for $Pm3m$ – $P4mm$ in the two end members (Fig. 2). $T_m$ values at five compositions given by Sanchez et al. [3] fall somewhat above this line and are not shown. The $P4mm$ – $Cm$ and $Cm$ – $Cc$ transitions in Pb(Zr0.52Ti0.48)O3 are accompanied by small dielectric anomalies (e.g. [52]), but there appears to be no analogous evidence for these in data reported for samples within the PZT–PFN binary being considered here [3, 48, 65, 68].

A further constraint on the topology of the binary system comes from the fact that it cuts the expected location of the room temperature MPB at two compositions, corresponding to $\sim 1$–7 and $\sim 69$–75 % PFN. These two points are shown in Fig. 2 as marking the position of the $P4mm$ – $Cm$ transition at room temperature, assuming that the stability field of the monoclinic structure extends into the ternary field.

A tricritical point, marking the change from continuous (Zr-rich compositions) to discontinuous (Ti-rich compositions) character for the ferroelectric transition, exists close to the 50:50 composition in PZT (Pb(Zr0.49Ti0.51)O3 [14, 15, 19, 73], between Pb(Zr0.55Ti0.45)O3 and Pb(Zr0.58Ti0.42)O3 [74]). It is not accidental that this occurs close to the MPB because the crossover between stability fields for tetragonal and rhombohedral structures is also determined by one of the fourth-order coefficients in the Landau 246 potential tending to zero ([75–77] and see Appendix of this paper). There is likely to be a line of tricritical points near the ternary MPB, and the ferroelectric transition in ceramics with compositions between Pb(Zr0.53Ti0.47)O3 and PFN is expected to be close to tricritical in character.

**Magnetic properties**

Rather less is known about magnetic transitions across the PT–PZ–PFN ternary. $T_N$ for the antiferromagnetic ordering transition in PFN diminishes from $\sim 143$ K with increasing PT content along the PT–PFN binary join and would extrapolate to 0 K at $\sim 13$ % PT [33]. From the same work [33], it appears that a magnetic anomaly attributed to a spin glass
transition \( T_g \approx 10–30 \text{ K} [78–86] \)) extends to at least 15 % PT. A closely similar pattern is seen with increasing PZ content along the PZ–PFN join in Li-doped samples [42]. There is, however, great variability between samples, and weak ferromagnetism has been reported both at room temperature and at temperatures up to \( \sim 530–580 \text{ K} [28, 86–89] \). Weak ferromagnetism was detected at room temperature in ternary compositions along the \( \text{Pb(Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3–\text{PFN} \) join by Sanchez et al. [3] and along the \( \text{Pb(Zr}_{0.44}\text{Ti}_{0.56})\text{O}_3–\text{PFN} \) join by Amonpattaratkit et al. [47]. It remains possible that the weak room temperature ferromagnetism in PFN and PZT–PFN is due to the presence of some minor impurity phase, but Kuzian et al. [90, 91] have shown that ferromagnetic ordering might occur in PFN, while Glinchuk et al. [4] have shown how a nanodomain structure of local chemical ordering could lead to ferromagnetism in PZT–PFN.

**B-site ordering**

Even though there appears to be no direct diffraction evidence for long-range B-site ordering of \( \text{Fe}^{3+} \) and \( \text{Nb}^{5+} \) in PFN, Mössbauer and NMR spectroscopy suggest a degree of short-range order or clustering [92–94]. Alternating Fe/Nb in three dimensions would change the symmetry of the cubic phase from \( Pm\bar{3}m \) to \( Fm\bar{3}m \) [95]. If this can occur during the preparation of end member PFN samples, the same local ordering might be expected in samples with compositions extending into the ternary system.

Besides affecting the consequent magnetic ordering, B-site order is an important potential influence on relaxor ferroelectric properties. The temperature of the maximum of the real part of the dielectric permittivity related to the ferroelectric transition in PFN is typically broad but independent of frequency [96–100]. It can be weakly dispersive in some samples [101–103], however, with variability of the local order responsible for relaxor as opposed to classical ferroelectric behaviour. Evidence for a temperature below which polar nanoregions (PNR’s) might be present is provided by acoustic emission (564–603 K [30]), thermal expansion data (\( \sim 690 \text{ K} [104] \)) and the onset of elastic softening (\( \sim 550 \text{ K} [28] \)). No information is yet available for local ordering in ternary PZT-PFN, but ceramics near the MPB have dielectric maxima related to the ferroelectric transition which are reported to be generally broad and independent of frequency [65, 67, 68, 70].

**Strain and elasticity**

Elastic and anelastic relaxation phenomena associated with phase transitions are due to coupling of the driving order parameter(s) with strain. There are as yet no data for strain relaxation effects in PZT–PFN multiferroics, but lattice parameters and elasticity data from the literature for \( \text{Pb(Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3 \) give a clear picture of what is expected for a sequence \( Pm\bar{3}m – P4mm–Cm–C \). A formal analysis of the spontaneous strains is given in the Appendix, and these are compared with PFN in Appendix Fig. 10. The cubic–tetragonal transition in \( \text{Pb(Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3 \) is accompanied by a tetragonal shear strain, \( \epsilon_4 \), amounting to \( \sim 3 \% \), in comparison with only \( \sim 0.3 \% \) for PFN. In both cases, the strain variations can be well represented as conforming to Landau tricritical (\( q^4(\tau – T) \)). The tetragonal-monoclinic transition is weakly first order and is accompanied by much smaller additional shear strains that are similar in form for both PZT and PFN. The \( Cm–C \) transition is accompanied principally by a small, negative volume strain. Even more obviously than for PFN, the \( Pm\bar{3}m – P4mm \) and \( P4mm–C \) transitions in \( \text{Pb(Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3 \) are quite distinct instabilities with different critical temperatures, implying that there are two separate driving mechanisms.

Changes in elastic properties have been studied extensively for PZT [44, 49, 105–109]. As expected for improper ferroelastic cubic–tetragonal and cubic–rhombohedral transitions with strong coupling between symmetry breaking shear strains and the order parameter, measurements at Hz and kHz frequencies on ceramic samples with compositions close to the MPB show large (\( \sim 50 \% \)) softening of the Young’s modulus, \( 1/S_{11} \), and shear modulus, \( G \) [44, 105–107, 109]. A sample doped with Nb has also shown the same pattern of elastic softening [110]. Characteristic peaks in acoustic loss, expressed in terms of the inverse mechanical quality factor, \( Q^{-1} \), show dispersion with respect to frequency and are attributed to the motion under stress of the ferroelastic twin walls [106, 107, 109, 111]. From the measurements of Bourim et al. [107] at Hz frequencies, it appears that the twin walls become pinned by
oxygen vacancies in the vicinity of ~400 K, below which the loss returns to low values.

There is a rounded minimum in the Young’s and shear moduli at temperatures corresponding to the expected location of the tetragonal–monoclinic transition in PZT [49, 105–109, 112]. The transition appears to be reversible for Pb(Zr0.52Ti0.48)O3 but displays a small hysteresis between heating and cooling at Pb(Zr0.535Ti0.465)O3 and Pb(Zr0.545Ti0.455)O3 [106, 109]. If there is any associated anomaly in Q−1, it is perhaps only a slight increase with falling temperature through the transition at both Hz and kHz frequencies [49, 105–107, 109]. By way of contrast, a poled sample of Pb(Zr0.52Ti0.48)O3 displayed a sharp minimum in the Young’s modulus measured at ~150 kHz [52, 60, 113, 114]. The difference is presumed to reflect a difference in microstructure, with the unpoled sample having a higher density of nanoscale twinning.

The octahedral tilting transition (R3m–R3c) in Zr-rich samples away from the MPB in PZT is accompanied by a small step-like softening of the Young’s modulus and a small peak in acoustic loss [44, 49, 108]. This is the expected pattern for a c-elastic, displacive transition with second-order character and weak strain/order parameter coupling. The loss peak measured at kHz frequencies remains discernible in the vicinity of the MPB, but its influence on the Young’s modulus is much harder to see [44, 49, 109]. The minimum in Young’s modulus is sharp when measurements are made on poled samples [52, 60, 113, 114]. A single measurement of longitudinal acoustic velocity through a sample of Pb(Zr0.53Ti0.47)O3 showed a small rounded minimum with a slight hysteresis [61]. In this case, the measuring frequency was not specified but is presumed to be in the MHz range.

Sample preparation and characterisation

The ceramic samples used in the present study with nominal compositions [PbZr0.53Ti0.47O3]1–x[PbFe0.5 Nb0.5O3]x, x = 0.6, 0.4, 0.3 were the same as those described in Sanchez et al. [3]. They are referred to below as PZTFN6, PZTFN4 and PZTFN3, respectively. As described in Sanchez et al. [3] and in more detail by Carpenter et al. [28] for PFN, they were prepared from oxide starting materials by a conventional solid-state reaction route. The final stage was heating of pressed pellets to 1250 °C (PZTFN4, PZTFN3) or 1100 °C (PZTFN6) at 10 °C min−1, annealing at this temperature for 4 h and cooling back to room temperature, again at 10 °C min−1. The resulting ceramic discs, ~9 mm in diameter and ~0.5–0.65 mm thick, were sawn into smaller pieces for the different measurements described below. An additional sample with x = 0.2 (PZTFN2) was prepared in a second batch. Ferroelectric hysteresis loops measured at room temperature for PZTFN2, PZTFN3 and PZTFN4 are given in Fig. 3a of Sanchez et al. [3].

A ceramic sample of PbZr0.53Ti0.47O3 (PZTFN0) was also prepared by a conventional solid-state route. PbO, ZrO2, TiO2 powders were mixed and calcined at 1000 °C for 2.5 h. The calcined powders were ground for 10 min and again ball milled for 1 h. Poly(vinyl alcohol) solution (1 wt%) was added to the calcined powder as a binder, and the powder was again dried in an oven at about 80 °C for 5 h. The dried powder was granulated by passing it through a mesh and pressed into a pellet. The pressed pellet was heat treated at 600 °C for the removal of organic binders followed by sintering at 1250 °C for 4 h. All the heating treatments were performed in air.

Average compositions, based on point analyses obtained for the final ceramic sample using a Cameca SX-100 electron microprobe, are given in Table 1. In general, the perovskite was homogeneous with respect to Fe and Nb, but with was some variation in Zr:Ti across individual grains. Several impurity phases were also detected in chemical map images. SX-100 electron microprobe, are given in Table 1. In particular, Fe2O3–Al2O3 with Al coming from the crucibles or ZrO2 and PbFe0.5 Nb0.5 O3 which has a stoichiometry close to that of pyrochlore, PbA4O7. The traces of W are presumed to reflect a difference in microstructure, with the unpoled sample having a higher density of nanoscale twinning.

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- Pb1(Zr0.21Ti0.47Fe3.42Al3.68W0.11)7.94O15.8,
- Pb1(Zr0.10Ti0.40Fe2.40Nb0.02Al2.63W0.12)5.67O10,
- Pb1(Zr0.05Ti0.45Fe2.70Nb0.05Al4.40W0.30)7.94O15

and

- Pb1(Zr0.19Ti0.22Fe0.26Nb0.27Al0.52W0.39)1.88O2.91,

in PZTFN2, PZTFN3, PZTFN4 and PZTFN6, respectively. These all belong essentially to the system PbO–Fe2O3–Al2O3 with Al coming from the crucibles or Al2O3 powder which was placed around the pellets to ensure an even temperature distribution. PZTFN2 contained some ZrO2 and PZTFN4 contained a second impurity, ~Pb1(Zr0.20Ti0.36Fe1.06Nb0.17Al1.35 W0.54)3.62O6.51, which has a stoichiometry close to that of pyrochlore, PbA4O7. The traces of W are presumed
to be from the WC ball mill. A small amount of excess PbO appears to occur along grain boundaries.

Higher resolution X-ray diffraction data than reported by Sanchez et al. [3] were obtained with a Bruker D8 Advance Bragg–Brentano diffractometer (PZTFN3, PZTFN2, PZTFN0) or a PANalytical Empyrean diffractometer (PZTFN6, PZTFN4). These revealed the presence of some impurity phase(s) at low concentrations perhaps up to a few %, as for PFN prepared in the same way [28]. The PZTFN2 sample, prepared separately, had a higher concentration of impurities and a second perovskite phase. Rietveld refinements [115] using the FULLPROF suite of programs [116] showed the dominant phase to be tetragonal perovskite with lattice parameters given in Table 2, consistent with bulk compositions being just to the PT side of the ternary MPB at room temperature (Fig. 1). Values of the tetragonal shear strain, ε_t, calculated from the lattice parameters, a and c, with an approximation for the cubic reference parameter a_o as (a^2c)^1/3, are also given in Table 2.

Magnetic hysteresis loops and first-order reversal curve (FORC) diagrams were obtained at room temperature using a Princeton Measurements Company alternating gradient magnetometer manufactured by Lake Shore Cryotronics, which is housed in the Nanopaleomagnetism Lab at the University of Cambridge. Hysteresis loops were measured using a saturating field of 1.8 T, a field step of 5 mT, and a time constant of 100 ms. FORC diagrams are obtained by plotting the FORC distribution (ρ), which is the mixed second derivative of the magnetisation with respect to the reversal and measurement fields [117, 118]. The FORC diagram is a contour plot of ρ in a space defined by B_c (coercive field) in the horizontal dimension and B_u (interaction field) in the vertical dimension. In effect, FORC diagrams can be thought
of as maps of the magnetic response of all particles in a sample in terms of coercivity and magnetic interaction field distributions [118]. This approach to characterization of magnetic samples is very useful in discriminating between components with different magnetic states and is widely used in rock and mineral magnetism and solid-state physics [118–121]. FORC diagrams were calculated from [237] 300 FORCs measured on each sample using a saturating field of 2.2 T, time constants of 100–300 ms, field steps of 4–6 mT, and maximum coercivities ($B_c$) of 1–1.95 T, depending on the characteristics of the hysteresis loops. The FORCs were processed with the program FORCinel [122] using the VARIFORC method for variable smoothing [123].

The magnetic hysteresis loops show small openings, indicative of a weakly ferromagnetic component present in all the samples (insets Fig. 3). The FORC diagrams are characterised by the presence of a low coercivity (0.05–0.1 T) magnetic component, implied by the strong maximum at low values of $B_u$ and $B_c$, vertical spreading, together with the pairing of the stronger positive and weaker negative areas and the displacement below the horizontal axis (Fig. 3). These features are indicative of discrete particles consisting of single magnetic domains with inter-particle magnetostatic interactions that are creating a net positive mean interaction field. The interactions are weaker in PZTFN2, PZTFN3 and PZTFN4, as shown by less vertical spreading and relatively minor displacement of the peak below the horizontal axis, compared to PFN and PZTFN6. PFN contains a second, high coercivity (~2 T) component, indicated by the ridge-like feature along the horizontal axis at high values of $B_c$ and the extended statistically significant area below the horizontal axis [28]. PZTFN6 exhibits a second, very low coercivity (<0.02 T) component, seen as a triangular positive feature near the origin, which is responsible for the constriction in the hysteresis loop.

### Experimental methods

**Resonant ultrasound spectroscopy (RUS)**

RUS data were collected using slightly irregular, but almost parallelepiped-shaped samples with dimensions and masses given in Table 2. The high-temperature (HT) RUS measurements were performed after the low temperature (LT) RUS measurements and the larger samples from the LT measurements were subdivided in-between these two experiments and hence the lower masses in Table 2 for the HT experiments. The instrument used for measurements above room temperature has been described by McKnight et al. [125] and uses Stanford electronics [126]. Temperature was determined with a thermocouple.

| Sample       | Dimensions of HT RUS and FORC samples (mm$^3$) | Mass of sample for HT RUS and FORC (g) | Mass of sample for LT RUS and SQUID 1 (g) | Mass of sample for SQUID 2 and heat capacity (g) |
|--------------|-----------------------------------------------|--------------------------------------|----------------------------------------|---------------------------------------------|
| PFN          |                                               |                                      |                                        |                                             |
| PZTFN6       | 4.0260(2) x 0.0124 x 2.950                      | 0.0216                               | 0.0393                                 | 0.01147                                      |
| PZTFN4       | 4.0362(2) x 0.0138 x 3.215                      | 0.0215                               | 0.0564                                 | 0.01382                                      |
| PZTFN3       | 4.038$^*$ x 0.011 x 3.022                       | 0.0131                               | 0.0650                                 | 0.00586                                      |
| PZTFN2       | 4.0126(1) x 0.0268 x 0.991                      | 0.1503/0.0402                        | 0.1503                                 | 0.0208                                       |
| PZTFN0       | 4.0573(2) x 0.0150 x 0.25                        | Irregular, ~3 x 2 x 0.25             | ~0.02                                  | ~0.02                                        |
| PbZr$_{0.52}$Ti$_{0.48}$O$_3$ | 0.0278$^*$                                      |                                      |                                        |                                             |

Values of $\epsilon_t$ for the end member compositions are taken from Appendix Fig. 10. Also given are the dimensions and masses of the samples used for RUS measurements at high temperature (HT) and masses of the samples used for low temperature (LT) RUS and in measurements performed in SQUID 1 and SQUID 2.

* Strains at room temperature from Carpenter et al. [28] for PFN and from Appendix for PZT

† Lattice parameters estimated from broadened (112)/(211) diffraction peak
located within a few mm of the sample, subject to an additional small calibration based on the transition temperature for the $\alpha - \beta$ transition in quartz (846 K), the cubic–tetragonal transition in BaTiO$_3$ (405 K) and the $R3m \rightarrow C2/c$ transition in Pb$_3$PO$_4$ (453.6 K). The helium flow cryostat used for measurements below room temperature has been described by McKnight et al. [127]. In each case, spectra were collected in heating and cooling cycles, generally in steps of 3, 5 or 10 K, with a settle time of 20 min for thermal equilibration at each temperature. The spectra were analysed offline using the software package Igor Pro (WaveMetrics). Selected resonance peaks were fit with an asymmetric Lorentzian function to obtain the peak frequency, $f$, and width at half maximum height, $\Delta f$. $f^2$ scales with the elastic modulus that determines the particular resonance mode and for most modes this is dominated by the shear modulus. In order to follow variations of the shear modulus over wide temperature intervals, it is sometimes necessary to combine data from different resonance peaks by scaling their values to overlap. The inverse mechanical quality factor, $Q^{-1}$, is a measure of acoustic loss and has been calculated as $\Delta f/f$. Values of $Q^{-1}$ measured in the low temperature instrument tend to be higher than those measured in the high-temperature instrument because the sample sits directly between the transducers rather than being separated from them by buffer rods.

**Temperature dependence of dielectric properties**

Dielectric measurements were made using an Agilent HP4294a Precision Impedance Analyzer, with the sample held in the same horizontal Netzsch furnace as used for the high-temperature RUS measurements. Electrodes were created on opposite sides of the RUS samples using high-temperature silver paste and these were connected by platinum wires to coaxial cables outside the furnace. The temperature and impedance analyzer were controlled using LabView software. Data were collected in both heating and cooling cycles, with a temperature ramp of 0.2 K min$^{-1}$ and each measurement taking approximately 10 s. The results are presented as capacitance and dielectric loss tangent. The capacitance is not calibrated, with some parasitic component expected due to some unshielded length of wire.

**Temperature dependence of magnetic properties**

Magnetic properties were measured in two different quantum design MPMS XL squid magnetometers, one in Cambridge (SQUID 1) and the other in Dresden (SQUID 2). Data were collected at low temperatures in both instruments, while high-temperature data were collected only in SQUID 2. In each case, the sample measured was the RUS sample, a portion of the RUS sample or a portion of the pressed pellet from which the RUS sample was taken. For the SQUID 2 measurements, the sample was held in an open quartz tube. For low temperature measurements, the sample was placed in an evacuated capsule and held in a straw.

The first magnetic investigation was carried out on SQUID 1 in order to study the magnetic behaviour under very low fields. This involved two sequences of data collection during heating from 5 K up to room temperature with the moment measured in the residual field of the magnet. The first measurement was preceded by cooling in “zero” field, labelled ZFC (i.e. cooling in the residual field of the magnet), while the second was preceded by cooling in a field of 20 kOe, labelled FC, from room temperature down to 5 K. These showed significant features that were absent in similar measurements run with probe fields of 0.01 kOe on heating, demonstrating that some part of the history-dependent behaviour in these materials has very low coercivity values. The magnetisation values were scaled to 1 at room temperature, as the magnitude and direction of the residual field were not controlled and the absolute value of the measured moment cannot readily be compared. In SQUID 1, magnetic hysteresis curves were also collected at selected temperatures during cooling with applied fields between $+50$ and $-50$ kOe.

In SQUID 2, both low temperature and high temperature measurements were performed using a more conventional zero field cooled-field cooled sequence, comprising cooling in the residual field of the SQUID, followed by measurement of the moment in 0.1 kOe applied field on heating (ZFC measurement), followed again by measurement in 0.1 kOe on cooling (FC measurement). This was most effective when performed in the full temperature range, from $\sim 5$ to $\sim 700$ K, although it required a change from the cryostat to the furnace and back. To determine the total evolution of the moment provided by the field,
Figure 4 PZTFN6. a RUS analysed data showing $f^2$ and $Q^{-1}$, with scaling applied to match frequencies at room temperature. b SQUID 2 temperature dependence of the magnetic moment between ~2 and 700 K under an applied field of 0.01 T, with triangular markers (one marker displayed per four data points) showing ZFC and FC data below room temperature; crosses (one marker displayed per two data points) show ZFC data above room temperature and FC data for the full temperature range. c SQUID 1 temperature dependence of magnetic moment measured in the residual field of the magnet between 2 and 300 K, with ZFC data scaled to match FC data at room temperature. d SQUID 1 magnetic hysteresis loops collected at selected temperatures in a cooling sequence (one marker displayed per four data points). e Capacitance and f dielectric loss at selected frequencies (one marker displayed per 200 data points).
the most reasonable approach was to do a ZFC measurement from 700 K to room temperature, then a FC measurement from 700 K to room temperature, followed by a FC measurement in the cryostat. Generally, this was combined with a ZFC/FC cycle in the cryostat alone, but the exact sequence differed between samples and is clear from an examination of the relevant figures, below. Hysteresis loops between −2 and −20 kOe were also performed at selected temperatures in SQUID 2 for PZTFN4 to check whether the loop opening closed at high temperatures.

Heat capacity

The heat capacity of an irregularly shaped piece of PZTFN3 with mass 0.00586 g, held in Apiezon H grease, was measured between 3 and 400 K by a relaxation method with the HC option of a Quantum Design model 6000 PPMS. Data were collected in three sequences on heating with temperature steps of 2–5 K and three pulses per temperature point.

Results

Variations with temperature of elasticity, dielectric and magnetic data are shown for PZTFN6–PZTFN0 in Figs. 4–9, respectively. They display a number of features in common:

(i) Reductions in $f^2$, corresponding essentially to precursor softening of the shear modulus, start at a temperature, $T_{ps}$, which is ≈100 K above the expected cubic–tetragonal transition. A narrow temperature interval of steep softening then follows, with a minimum that is generally not seen due to strong attenuation. Below the temperature where this steep softening ends, $T_{cRUS}$, there are further relatively minor variations and these are followed at the lowest temperatures by a concave-up pattern of stiffening.

(ii) The first increase in $Q^{-1}$ with falling temperature, marking the onset of acoustic loss relating to the phase transition, occurs at a temperature, labelled as $T^*$ (see Table 3), which is ≈30–60 K above $T_{cRUS}$. There is then a 50–100 K interval in which the attenuation can be sufficiently high that the resonance peaks disappear from the RUS spectra (superattenuation). Below this interval, $Q^{-1}$ remains relatively high until the lowest temperatures, but with minor peaks that differ between samples.

(iii) A broad, asymmetric and frequency-independent peak occurs in capacitance at a temperature, $T_m$ (see dashed lines in Figs. 4–9). This is clearly related to the ferroelectric transition and is similar to the variation in dielectric constant observed for other ceramic samples with nearby compositions in the ternary system [48, 65, 67, 68, 70].

(iv) Slight stiffening with falling temperature accompanied by hysteresis between heating and cooling occurs between ~200 and ~250 K in samples with intermediate compositions and appears to correspond with the tetragonal–monoclinic transition.

(v) Magnetic hysteresis loops all show a small opening at room temperature and below, indicative of a weak ferromagnetic moment. Magnetisation data show that this moment tends to zero in the vicinity of 500 K. There is no overt evidence for a magnetic transition below room temperature, but there are additional anomalies in the data for all three samples below ~50 K. The high-temperature ferromagnetism is most likely due to the impurity phases but the low temperature effects are more likely to be intrinsic to the perovskite.

Values of $T_{ps}$, $T_{cRUS}$, $T^*$ and $T_m$ are listed in Table 3.

PZTFN6

Results for $f^2$ and $Q^{-1}$ from the RUS spectra of PZTFN6 are shown in Fig. 4a. Analysed peaks in the high-temperature spectra had frequencies of 230 and 650 kHz at room temperature. Resonances from the low temperature spectra had frequencies of ~66 and ~400 kHz. Other peaks were used to refine the variation of $Q^{-1}$ above the high-temperature transition point. The onset of softening with falling temperature, $T_{ps}$, is at ~650 K (see Fig. 2a). An increase in $Q^{-1}$ starts at ~510 K, and the interval of superattenuation (no detectable resonances) is ~410–490 K. A shallow minimum occurs in $f^2$ at ~325 K, and there is a distinct hysteresis between heating and
PZTFN4.  

**Figure 5**  

**a** RUS analysed data showing $f^2$ and $Q^{-1}$, with scaling applied to match $f^2$ values at room temperature.  

**b** SQUID 2 temperature dependence of the magnetic moment between $\sim 2$ and 700 K measured under an applied field of 0.01 T.  

**c** SQUID 1 temperature dependence of magnetic moment measured in the residual field of the magnet between 2 and 300 K, with ZFC data scaled to match FC data at room temperature.  

**d** SQUID 1 magnetic hysteresis loops collected at various temperatures (one marker displayed per four data points).  

**e** Capacitance and dielectric loss at selected frequencies (one marker displayed per 200 data points).
Figure 6 PZTFN3. **a** RUS analysed data showing $f^2$ and $Q^{-1}$, with scaling applied to match $f^2$ values at room temperature. **b** SQUID 2 temperature dependence of the magnetic moment between 2 and 700 K under an applied field of 0.01 T, with triangular markers (one marker displayed per two data points) showing ZFC and FC data below room temperature; crosses (one marker displayed per two data points) show ZFC data above room temperature and FC data for the full temperature range. Note that the high-temperature ZFC result indicate that the probe field of 0.01 T is above the coercive field for this sample above 300 K. **c** SQUID 1 temperature dependence of magnetic moment measured in the residual field of the magnet between 2 and 300 K, with ZFC data scaled to match FC data at room temperature. **d** SQUID 1 magnetic hysteresis loops collected at various temperatures (one marker displayed per four data points). **e** Capacitance and **f** dielectric loss at selected frequencies (one marker displayed per 200 data points).
cooling centred on \( \sim 220 \) K. \( Q^{-1} \) has relatively high values below the superattenuation interval and shows small peaks at \( \sim 165 \) K and below \( \sim 100 \) K, which are accompanied by changes in slope of \( f^2 \), before falling off to low values at the lowest temperatures. (The apparent hysteresis near 100 K is an artefact arising from difficulties in measuring weak peaks).

Measurements of magnetic moment as a function of temperature at low and high temperature in SQUID 2 (Fig. 4b), in residual field in SQUID 1 (Fig. 4c) and as a function of field in SQUID 1 (Fig. 4d) give patterns that are similar to those seen for PFN [28]. Significant curvature of the reciprocal susceptibility in the temperature-dependent magnetic data precludes Curie–Weiss analysis. There is a steep increase in the low applied field magnetic moment (Fig. 4c) in the field cooled data below \( \sim 20 \) K as well as a separation between FC and ZFC data across the temperature range examined in that measurement. The measured magnetic moments do not show evidence for an antiferromagnetic transition in either low or high field conditions. Higher field, temperature-dependent magnetic data from SQUID 2 (Fig. 4b) clearly show the ferromagnetic transition occurring at \( \sim 560 \) K, as well as replicating the 20 K anomaly seen in the low-field data. Magnetic hysteresis loops show a small opening at every temperature. The change in shape of the loop at 5 K relative to that at 30 K suggests that there is some kind of transition between the two.

The dielectric data (Fig. 4e, f) show a broad peak in capacitance at \( \sim 500 \) K. The amplitude varies systematically with frequency but \( T_m \) does not, and there is a very slight maximum in loss tangent, \( \tan\delta \).

Although the form of variations of both capacitance and \( \tan\delta \) remains the same between heating and cooling, there is a marked reduction in their absolute values in the cooling sequence relative to heating. A steep reduction in capacitance occurs just below \( T_m \) at \( \sim 484 \) K, and there is a further subtle maximum at \( \sim 380 \) K. Neither of these features appears to correlate systematically with variations in \( \tan\delta \) but \( f^2 \) would extrapolate to its lowest value at \( \sim 480 \) K \( (T_{\text{cRUS}}) \).

### PZTFN4

Results for \( f^2 \) and \( Q^{-1} \) from the RUS spectra of PZTFN4 are shown in Fig. 5a. \( f^2 \) values are again a compilation from different resonances, scaled to match up at room temperature (peaks from the high-temperature spectra at 330 and 180 kHz and a peak from the low temperature spectra at 81 kHz). The onset of softening with falling temperature ahead of the cubic–tetragonal transition occurs at \( \sim 700 \) K, superattenuation occurs in the interval \( \sim 440–550 \) K, the shallow minimum in \( f^2 \) is at \( \sim 250 \) K, the slight hysteresis is centred on \( \sim 190 \) K, and a steep upturn occurs below \( \sim 85 \) K. \( Q^{-1} \) remains high below the superattenuation interval and only diminishes below \( \sim 40 \) K. Well-resolved \( Q^{-1} \) values at low temperatures reveal a small Debye-like peak at \( \sim 165 \) K and another maximum at \( \sim 70 \) K.

Higher field temperature-dependent magnetic data from SQUID 2 (Fig. 5b) clearly show the ferromagnetic transition occurring at \( \sim 450 \) K, with a tail up to \( \sim 500 \) K, as well as a steep upturn in magnetisation below \( \sim 45 \) K. Although most of the low temperature behaviour is considered in terms of some paramagnetism, there is a divergence in trends of the evolution of FC and ZFC magnetisation in the low-field data below \( \sim 150 \) K (Fig. 5c). The higher field data do not show any anomaly at 160 K. The low field, SQUID 1, FC data go sharply in the opposite direction to the ZFC data at \( T < 15 \) K; a maximum occurs at \( \sim 50 \) K in the FC data and at \( \sim 160 \) K in the ZFC data. Significant curvature of the reciprocal susceptibility precludes any Curie–Weiss analysis. Magnetic hysteresis loops from SQUID 1 (Fig. 5d) show small openings. Also for the 300 and 400 K curves taken on SQUID 2, the opening gets significantly smaller at 400 K but is still visible. The change in shape of the loop at 5 K relative to that at 30 K again suggests that there is some kind of transition between the two.
Figure 8 PZTFN2. a RUS analysed data showing $f^2$ and $Q^{-1}$, with scaling applied to match $f^2$ values at room temperature. b SQUID 2 temperature dependence of the magnetic moment between ~5 and 700 K under an applied field of 0.005 T. c SQUID 1 temperature dependence of magnetic moment measured in the residual field of the magnet between 2 and 300 K, with ZFC data scaled to match FC data at room temperature. d SQUID 1 magnetic hysteresis loops collected at various temperatures (one marker displayed per four data points). e Capacitance and f dielectric loss at selected frequencies (one marker displayed per 200 data points).
The dielectric data (Fig. 5e,f) show a broad peak in capacitance at $\sim 550$ K. The amplitude again varies systematically with frequency, but $T_m$ does not, and there are slight anomalies in the loss tangent, $\tan\delta$. At low frequency and high temperature, an additional anomaly is most likely due to the influence of conductivity.

**PZTFN3**

Results for $f^2$ and $Q^{-1}$ from the RUS spectra of PZTFN3 are shown in Fig. 6a. $f^2$ values are a compilation from peaks from the high-temperature spectra with frequencies of 184, 219, 310, 590, 593 kHz at room temperature, and a peak from the low temperature spectra with frequency 510 kHz. The onset of elastic softening is above the highest temperature reached, $\sim 700$ K, and the superattenuation interval is $\sim 450$–$560$ K. Resonance peaks were detectable in the high-temperature RUS spectra below $\sim 450$ K but were too weak to allow reliable fitting. The shallow minimum in $f^2$ appears to occur at $\sim 410$ K. This sample has the most clearly defined hysteresis in the whole series, with a small step (increasing stiffness with falling temperature) occurring at 205 K during cooling, and at 240 K during heating. There is also a clear break in slope at $\sim 165$ K and the onset of relatively steep stiffening with falling temperatures occurs at $\sim 65$ K. $Q^{-1}$ remains high below room temperature, reducing steadily with falling temperature and with a peak at $\sim 165$ K. There may be a broad peak in $Q^{-1}$ at around 50–70 K, but the data are noisy.

Higher field temperature-dependent magnetic data from SQUID 2 (Fig. 6b) clearly show the ferromagnetic transition occurring at $\sim 500$ K, and a steep upturn in moment below $\sim 22$ K. Low-field temperature-dependent magnetic data from SQUID 1 (Fig. 6c) again show significant differences between FC and ZFC values, but the additional anomalies below $\sim 25$ K are not observed. ZFC data have slightly reducing moment with falling temperature below $\sim 50$ K. Magnetic hysteresis loops from SQUID 1 (Fig. 6d) show a small opening at every temperature. As with the other samples, the change in shape of the loop at 5 K relative to that at 30 K suggests that there is some kind of transition between the two.

Figure 9 PZTFN0. a RUS data. Different pieces of sample were used for the low and high-temperature experiment, but they came from the same original pressed pellet. $f^2$ values have been scaled to match at room temperature on heating. (The break in absolute $Q^{-1}$ values at 300 K is an artefact arising from the different experimental set up for low and high-temperature RUS instruments). b Capacitance and c dielectric loss at selected frequencies (one marker displayed per 200 data points).
Capacitance variations show a frequency-independent maximum at \( \sim 572 \, \text{K} \) (Fig. 6e). This is accompanied by a minimum in tan\( \delta \) measured at 1.1 and 12.7 kHz and a maximum in tan\( \delta \) measured at 1 MHz (Fig. 6f). The steep drop in capacitance at 559 K is more obvious than for either PZTFN6 or PZTFN4 and is accompanied by a steep change also in tan\( \delta \). In contrast with the data for PZTFN6 and PZTFN4, there are almost no differences in the values of either capacitance or dielectric loss between heating and cooling. The more subtle maximum in capacitance occurs at \( \sim 390 \, \text{K} \).

Specific heat data were collected in heating sequences for PZTFN3 in order to check for independent evidence of a tilting transition. They show a smooth variation up to 155 K followed by a series of small anomalies, in particular at \( \sim 175, \sim 217, \sim 300 \) and \( \sim 338 \, \text{K} \) (Fig. 7). The drop with increasing temperature between 155 and 175 K resembles the typical form associated with a second-order phase transition, and its location correlates with the small anomalies seen in the RUS data at \( \sim 165 \, \text{K} \). The irregularity at 210 K is close to the measured thermal hysteresis, but those at 300 and 338 K fall in regions of very high Q\(^{-1} \).

### PZTFN0

Results for \( \vec{\rho} \) and Q\(^{-1} \) from the RUS spectra of PZTFN0 are shown in Fig. 9a. \( \vec{\rho} \) values are from a peak with frequency 672 kHz at room temperature in the high-temperature spectra and a peak at 108 kHz from the low-temperature spectra. Elastic softening starts above the highest temperature reached, i.e. above 700 K, and reaches a well-defined minimum at \( \sim 640 \, \text{K} \). The total softening amounts to \( \sim 45 \% \). Subsequent variations are small, with shallow minima at \( \sim 220 \) and \( \sim 360 \, \text{K} \). There is a clear hysteresis between heating and cooling below \( \sim 350 \, \text{K} \) in the high-temperature data for \( \vec{\rho} \). High-temperature data for Q\(^{-1} \) come from peaks with frequencies of 540 kHz (cooling) and 310 kHz (heating). High loss occurs between \( \sim 700 \) and 550 K, but it was possible to observe resonance peaks reasonably clearly throughout this interval, and there is then a smaller maximum at \( \sim 505 \, \text{K} \). Data for Q\(^{-1} \) at low temperatures are from the 108 kHz peak and have well-defined Debye-like maxima at \( \sim 190 \) and \( \sim 260 \, \text{K} \). There is a trend of increasing stiffness and decreasing loss below \( \sim 200 \, \text{K} \) but no sign of the steep upturn below 50–100 K seen in data for the ternary PZTFN samples.

### PZTFN2

Results for \( \vec{\rho} \) and Q\(^{-1} \) from the RUS spectra of PZTFN2 are shown in Fig. 8a. The \( \vec{\rho} \) values are a compilation from a resonance peak in the high-temperature spectra which had frequency 162 kHz at room temperature, the same peak in the low-temperature spectra and another resonance in the low-temperature spectra which had frequency 80 kHz at room temperature. The onset of elastic softening with falling temperature is at \( \sim 820 \, \text{K} \), there is a relatively sharp minimum at \( \sim 575 \, \text{K} \), a rounded minimum at \( \sim 110 \, \text{K} \) and steep stiffening below this. Q\(^{-1} \) starts to increase below \( \sim 635 \, \text{K} \), and the strongest attenuation is between \( \sim 500 \) and \( \sim 660 \, \text{K} \). Q\(^{-1} \) values remain relatively high down to \( \sim 150 \, \text{K} \), below which there is a distinct peak at \( \sim 60 \, \text{K} \). Weak ferromagnetism evident from the field cooled data extends up to \( \sim 500 \, \text{K} \) (Fig. 8b), but there is no overt evidence for an anti-ferromagnetic transition at lower temperatures (Fig. 8b, c). Open hysteresis loops extend at least from room temperature down to 5 K with a clear increase in the maximum magnetisation below 30 K (Fig. 8d). The asymmetric maximum in the dielectric constant is at \( \sim 596 \, \text{K} \). This value of T\(_m\) is independent of frequency though the amplitude reduces with increasing frequency and shows some hysteresis (Fig. 8e). There is a further increase in amplitude with increasing temperature at the lowest frequencies and the ferroelectric transition is marked also by an anomaly in the dielectric loss (Fig. 8f).

### Table 3

Values of the temperature at which precursor elastic softening starts, T\(_{ps}\), Q\(^{-1}\) starts to increase, T\(^*\), the steep reduction of \( \vec{\rho} \) ends, T\(_{cRUS}\), and the dielectric constant or capacitance has a maximum, T\(_m\).

| Sample   | T\(_{ps}\) (K) | T\(^*\) (K) | T\(_{cRUS}\) (K) | T\(_m\) (K) |
|----------|---------------|-------------|-----------------|-------------|
| PZTFN0   | 820           | 635         | 575             | 596         |
| PZTFN2   | 700           | \(\sim 580\) | 544             | 555         |
| PZTFN3   | 650           | 510         | 480             | 500         |
| PZTFN4   | 550           | 430         | 355             | 377         |

* Values for PFN are from Carpenter et al. [28]
As with intermediate members of the solid solution, the maximum in capacitance occurs a few degrees above the minimum of $T_c$ ($T_{\text{CRUS}} \approx 651$, $T_m = 665$ K). The steep fall in capacitance occurs at $\sim 655$ K and $\tan \delta$ has an anomaly in the same temperature range (Fig. 9c).

**Discussion**

The rounded maximum in capacitance and lack of frequency dependence for $T_m$ are closely similar to reported results for the dielectric properties of other PZT–PFN ceramics [48, 65, 67, 68, 70]. Minor impurity phases do not appear to affect the main conclusions which can be drawn from elastic and dielectric properties measured at a macroscopic scale, but it would be incautious to relate any of the observed ferromagnetic properties to the perovskite.

From the perspective of strain and elasticity, intermediate members of the PZT–PFN solid solution show features typical of a classical improper ferroelastic phase transition followed by more complicated structural evolution that can be understood in terms of interaction of multiple order parameters. There is clearly strong coupling between strain and the ferroelectric order parameter. No evidence has been found for magnetoelastic effects.

**Improper ferroelastic transition**

The ferroelectric transition is marked by a broad, asymmetric peak in capacitance and, within reasonable experimental uncertainties, values of $T_m$ fall on a linear trend between the known cubic–tetragonal transition temperatures of Pb(Zr0.53Ti0.47)O3 and PFN (Fig. 2). A few degrees below this is a steep decline in the capacitance and a few degrees lower still is the temperature at which the steep elastic softening ceases. The pattern is similar to that observed from a sample of Pb(Zr0.52Ti0.48)0.975Nb0.025O3 for which heat capacity was also measured and the main peak in enthalpy change reported to occur at $\sim 24$ K below $T_m$ [128]. Taking the transition point, $T_c$, as being marked by the maximum in heat capacity would imply that the maximum in dielectric constant occurs above $T_c$ while the end of the steep softening occurs at or just below $T_c$.

Differences between the dielectric and elastic properties reflect differences between proper ferroelectric and improper ferroelastic character. Application of an ac electric field produces, predominantly, reversals in the orientation of electric dipoles and displacement of $180^\circ$ twin walls, whereas a dynamic stress field induces, predominantly, displacements of the $90^\circ$ twin walls in a tetragonal crystal. The differences between $T_m$ and $T_{\text{CRUS}}$ are also likely to relate to the longer length scale of correlations mediated by strain in comparison with correlations mediated by polarisation.

The interval just below $T_c$ is not recorded in the RUS data due to superattenuation, but the general form of softening of the shear modulus is consistent with classical relaxation effects of linear/quadratic strain/order parameter coupling. From consideration of the phase diagram, the pattern is expected to be that of a tricritical transition. The steep and nonlinear stiffening with falling temperature below $T_c$ is characteristic of tricritical character, as seen, for example, in association with tilting transitions in SrZrO3 [129], KMnF3 [130, 131], BaCeO3 [132] and quartz [125]. Also as expected in this context, there is a correlation between the magnitudes of the reduction in $\rho$, measuring softening of the shear modulus, and the magnitudes of the tetragonal shear strains. In Pb(Zr0.52Ti0.48)O3 $\varepsilon_t$ reaches $\sim 0.03$ (Appendix Fig. 10a) and the softening in PZTFN0 amounts to at least 40 %. (The shear modulus of Pb(Zr0.54Ti0.46)O3 softens by $\sim 60\%$ [109].) For PFN $\varepsilon_t$ reaches $\sim 0.002$ and the amount of softening is $\sim 35\%$ [28]. The corresponding strains and softening for intermediate members of the solid solution are $\sim 0.01$ (Table 2) and $\sim 40–50\%$ (Figs. 4a, 5a, 6a, 8a).

**Precursor softening**

Precursor elastic softening occurs from about $\sim 100$ K above the transition point across the entire solid solution (Fig. 2). If this is due to fluctuations of the soft mode, it would be expected to fit with a phenomenological description of the form

$$\Delta C_{ik} = A_{ik}(T - T_c)^{-\kappa},$$

(1)

where $\Delta C_{ik}$ is the amount of softening of single crystal elastic constants away from the trend for the cubic parent structure and $A_{ik}$ are material constants. The value of the exponent $\kappa$, between 1/2 and 2, depends on the anisotropy and dispersion of soft branches round the critical point of the soft mode [133–137] as has been found for precursor softening.
in SrTiO$_3$, LaAlO$_3$ and KMnF$_3$, for example [138–140].

If, on the other hand, the softening is due to relaxor-like freezing processes, it would be better represented by a Vogel–Fulcher equation

$$
\Delta C_{ik} = A_k \exp \left( \frac{E_a}{T - T_{VF}} \right),
$$

where $E_a$ is an effective activation energy and $T_{VF}$ is the zero-frequency freezing temperature. This was found to provide good descriptions of precursor softening of the shear modulus in PbMg$_{1/3}$Nb$_{2/3}$O$_3$ [141] and PbSc$_{0.5}$Ta$_{0.5}$O$_3$ [142], and it also describes softening ahead of the cubic–tetragonal transition in BaTiO$_3$ [143]. These models have been tested for PZT–PFN samples (Fig. 2). Kim et al. [74] showed that it couples strongly with acoustic modes immediately below the transition point. The microscopic origin of the central peak is understood as being from polarisation fluctuations which slow down as the transition point is approached with increasing or decreasing temperature. Development of a central peak is characteristic of relaxors [145], and observations by inelastic neutron scattering or Brillouin scattering should also provide closer insights into the nature of dynamic microstructures in PZT–PFN. The onset of increasing $Q^{-1}$ labelled as $T^*$ represents the temperature at which a strain-coupled microstructure starts to relax on a time scale of $\sim 10^{-5}$–$10^{-6}$ s and might represent the onset of a quasi-static tweed microstructure.

Twin wall dynamics and evidence for local strain heterogeneity

High acoustic attenuation in a temperature interval of $\sim 100$ K through and below the cubic–tetragonal transition is due to mobile ferroelastic twin walls and has been characterised at lower frequencies by Bourim et al. [107]. They observed two Debye loss peaks associated with pinning of the twin walls, probably by oxygen vacancies. Extrapolation of Arrhenius solutions for the frequency and temperature dependence would put the equivalent freezing process near 800 K when measured at $\sim 500$ kHz, however, implying that the same loss mechanism will not be detected in RUS data. It has been argued elsewhere, firstly, that displacements of ferroelastic twin walls can occur by at least two mechanisms, the advance/retraction of needle tips or the sideways migration of small ledges, and, secondly, that the latter will dominate under the relatively low stress and high-frequency conditions characteristic of RUS measurements [138, 146, 147]. On this basis, the low-frequency Debye peaks would be due to freezing of the needle tip motion, while the loss mechanism responsible for the superattenuation observed here is motion of ledges along the twin walls.

It is notable that there is no discrete Debye loss peak of the type seen for $Q^{-1}$ at $\sim 110$ K in PIN–PMN–PT [148] which could be indicative of a discrete freezing process for the mobile twin walls. Instead, relatively high values of $Q^{-1}$ continue to lower temperatures and aspects of the ferroelastic microstructures must remain mobile down to at least $\sim 50$ K. The steep increase in $f^2$ below $\sim 80$ K and a decline in values of $Q^{-1}$ only below $\sim 40$ K, which occurs in PZT–PFN samples (Figs. 4a, 5a, 6a), has been seen also in PFN [28] and in Pb(Zr$_{0.55}$Ti$_{0.45}$)$_3$O$_3$ (PFN) [149]. This appears to be a signature for freezing of defects which are coupled to shear strains and which have a spectrum of relaxation times, as would occur in a material with significant local strain heterogeneity. Some of the irregularity of the structural evolution, in comparison with materials which have single structural, magnetic or ferroelectric transitions, seems to correlate with the irregular pattern of small anomalies in heat capacity seen for PZTFN3 in the temperature interval $\sim 180–400$ K (Fig. 7). PFN itself is known to have a tweed microstructure over a wide temperature interval [150].

Defect dynamics at high temperatures

Irreversibility and the high dielectric loss above the transition temperature for each of the PZT–PFN samples do not appear in the elasticity data and are
therefore attributed to defects which are not coupled with strain. The sensitivity to heating in air implies that the concentrations of Fe²⁺ and oxygen vacancies are important in this and that some oxidation/reduction occurs at the highest temperatures. Furthermore, the irreversible changes depend on the total iron content in that they are substantial in PTZFN6 and PTZFN4 but do not occur in PTZFN3. The loss mechanism perhaps relates to conductivity at grain boundaries, as discussed for PFN by Raymond et al. [98, 99]. Frequency-dispersive dielectric properties unrelated to the phase transitions have also been attributed to a conduction mechanism depending on partial reduction of Fe³⁺ to Fe²⁺ [48, 65, 68].

Multiple instabilities

The first-order transition between tetragonal (P4mm) and monoclinic (Cm) structures in PZT samples with compositions close to the MPB is recognised by a rounded minimum in the Young’s modulus and a hysteresis of up to ~100 K between heating and cooling [106, 109]. A comparable hysteresis is seen, as expected, near 300 K in the high-temperature RUS data for PZTFN0 (Fig. 9a). The same pattern is not seen in the data for PZTFN2 (Fig. 8a) because the actual Zr:Ti of this sample, ~49:51, puts it further from the MPB, but it seems safe to attribute the hysteresis in f² between heating and cooling near 200 K for PZTFN6, PZTFN4 and PZTFN3 to the same transition. Estimates of the transition temperatures produce a boundary in the binary phase diagram which is consistent with the estimated position of the ternary MPB at room temperature (Figs. 1, 2). The rounded minimum of the Young’s modulus and shear modulus of PZT [49, 105–107, 109], becomes sharper in poled ceramics with compositions Pb(Zr₀.₅₁₅Ti₀.₄₈₅)O₃ and Pb(Zr₀.₅₂Ti₀.₄₈)O₃ [52, 60, 113, 114], though hysteresis in the present study on ternary compositions occurs at temperatures below the minimum in f². In none of the published data for PZT [44, 49, 105–107, 109], or in the present study, is there any evidence of the transition being accompanied by a significant anomaly in acoustic loss. Nor is there any precursor softening as it is approached from either side. It therefore appears that the weakly first-order transition is between structures with only slightly different shear moduli, and without any additional effects associated with strain/order parameter relaxation.

Strain analysis for Pb(Zr₀.₅₂Ti₀.₄₈)O₃ in Appendix has been used to imply that the transition sequence Pm3m → P4mm → Cm involves two separate instabilities with different order parameters. The effect of two separate order parameters is seen in SrZrO₃, where the sequence Pm3m → I4/mcm → Imma → Pnma is due to tilting and involves two order parameters with different (R-point and M-point) symmetries. The two M-point structures, I4/mcm and Imma, differ only in the combination of non-zero components, while the Pnma structure has both tilts. RUS measurements give minima in shear and bulk moduli at the I4/mcm → Imma transition, but only stiffening at the Imma → Pnma transition [129]. In BaTiO₃, the sequence P4mm → Amm2 → R3m involves only changes in orientation of a single (I′-point) order parameter and the two transitions give sharp minima in the shear modulus [147]. The evidence of stiffening associated with development of a second tilt system is that interactions between two separate driving order parameters hinder the strain relaxation mechanism responsible for elastic softening at displacive transitions when measured at high frequencies and with low applied stress. If this is the case, stiffening below the tetragonal–monoclinic transition rather than a sharp minimum, as observed here, would provide a further argument in favour of the monoclinic structure being stabilised by two separate order parameters with different critical temperatures. In this context, it is interesting to note the close similarity between order parameter evolution for Pb(Zr₀.₅₂Ti₀.₄₈)O₃ indicated by the strain analysis in Appendix Fig. 10b and the evolution of two separate order parameters calculated from first principles by Kornev et al. [54].

Tilting transition

The temperature for a tilting transition will depend, qualitatively, on the average radii of cations on the crystallographic B-site. This decreases with increasing substitution of Ti⁴⁺ (~0.61 Å) for Zr⁴⁺ (~0.71 Å) across the PZT solid solution and is ~200 K when the average reaches ~0.67 Å at Pb(Zr₀.₅₃Ti₀.₄₇)O₃ in the phase diagram of Cordero et al. [44] (ionic radii from [151]). The average of Fe³⁺ (~0.65 Å) and Nb⁵⁺ (~0.64 Å) is close to, but slightly lower than the average for the B-site cations in Pb(Zr₀.₅₃Ti₀.₄₇)O₃, so the tilting transition would be expected to extend
along the PZT–PFN join at progressively lower temperatures with increasing PFN content.

Location of the tilting transition in elasticity data collected at kHz frequencies is possible through the existence of a small anomaly in modulus and a peak in the acoustic loss [44, 49, 106, 109]. For PZTN0, the expected $Cm$–$Cc$ transition temperature is ~200 K, and this is marked by an increase in $Q^{-1}$, the end of softening and onset of stiffening (Fig. 9a). There is no separate evidence for the origin of the small Debye-like peak in $Q^{-1}$ near 165 K in all three of the PZT–PFN samples being due to octahedral tilting but, in the case of PZTFN3, at least, it is accompanied by a slight break in slope of $f^{2}$ (Fig. 6a) and an anomaly in heat capacity (Fig. 7). By analogy with the small loss anomaly seen in unpoled PZT close to the MPB [44, 49, 106, 109], it may correspond to the $Cm$–$Cc$ tilting transition.

A striking feature of the elastic anomalies associated with the R3m–R3c transition at Zr-rich compositions in PZT shown by Cordero et al. [49] is that they have the typical pattern of softening and loss associated with linear/quadratic strain/order parameter coupling in other perovskites. Close to the MPB, however, this signature essentially disappears, implying that the strain relaxation no longer occurs. By analogy with other systems, this provides further evidence for strain heterogeneity on a mesoscopic length scale. For example, a tilting transition in La$_{0.6}$Sr$_{0.1}$TiO$_3$ with cation/vacancy order is accompanied by changes in lattice parameters which represent normal spontaneous strains. The tilting transition still occurs if the cations and vacancies are disordered, but development of the long-range macroscopic strain is disrupted by the influence of heterogeneous strains on a unit cell scale [152]. Cation disorder, an adaptive microstructure of nanodomains and/or tweed would contribute to similar local strain heterogeneity in PZT–PFN and have the same effect in suppressing the macroscopic strain without suppressing the tilting transition itself.

**Magnetism and magnetoelastic behaviour**

There is no evidence in any of the dielectric, magnetic or elasticity data presented here that the antiferromagnetic ordering in PFN ($T_N$ ~ 150 K) extends across to PZT–PFN compositions. Magnetic hysteresis loops in the PZT–PFN samples show small openings at every temperature, but values of the coercivity and remnant moment at room temperature vary between samples. This weak ferromagnetism extends up to ~ 500-600 K and is most likely due to the impurity phases, though some contributions might also come from variable concentration of oxygen vacancies and, hence, the possible presence of Ti$^{3+}$, in the vicinity of grain boundaries. While the FORC analysis also indicates properties that are not uniform, there is a systematic trend observable in the diagrams, which suggests that inter-particle magnetostatic interactions (responsible for the vertical spreading and peak displacement below the horizontal axis) increase going from PZTFN2 to PFN (Fig. 3). It appears that the single domain particles are more randomly dispersed in PZTFN2, PZTFN3 and PZTFN4, while in the PFN-rich samples they are packed closer together and are arranged in a specific configuration, which results in a local anisotropy that gives rise to the positive mean interaction field.

On the other hand, the magnetic data for PZT–PFN show a distinct change in properties between 5 and 30 K, which is more likely to be intrinsic to the perovskite. In particular, the moments in applied field increase with falling temperature and simultaneously the coercive field for the small loop openings decrease for all the samples. There is a systematic lowering of the measured saturation magnetization, given in $\mu_B$ Fe$^{-1}$, at both low and high temperature upon addition of PFN. This goes from ~2 $\mu_B$ Fe$^{-1}$ for PZTFN2 to ~0.5 $\mu_B$ Fe$^{-1}$ for PZTFN6 and ~0.2 $\mu_B$ Fe$^{-1}$ for pure PFN. The pattern of evolution of the magnetic moment between FC and ZFC measurements is not totally consistent between samples, however. The origin of the low temperature anomalies is presumed to be essentially the same as the ordering which gives weak ferromagnetism in PFN and occurs within crystals which are now believed to have significant local strain heterogeneity. If there is even weak magnetoelastic coupling, a spin glass type of magnetic ordering and glassy strain could be interdependent.

**Multiferroicity**

The PZT–PFN samples produced for this study are truly multiferroic in displaying ferroelasticity, ferromagnetism and ferroelectricity to high temperatures. It seems likely that the impurity phases are responsible for the ferromagnetism, but this could still contribute significantly to the overall multiferroicity. The
magnetic field from a strongly ferromagnetic impurity phase present even in small proportions would influence the magnetic properties of the perovskite. Conversely, electrostriction from the perovskite is likely to influence the magnetic properties of the impurity. In this sense, samples with chemical and structural heterogeneity could turn out to have advantageous multiferroic properties which remain to be explored.

Conclusions

The elastic and anelastic properties of perovskites with compositions close to the ternary MPB of PbZrO₃-PbTiO₃-PbFe₀.₅Nb₀.₅O₃ are dominated by large softening of the shear modulus associated with the $Pm3m \rightarrow P4mm$ transition and high acoustic attenuation in a temperature interval of $\sim 100$ K below the transition point due to the mobility of ferroelastic twin walls. In this respect, the tetragonal ferroelectric structure has all the characteristic features of a typical improper ferroelastic. Evidence for a first-order transition, provisionally attributed to $P4mm \rightarrow Cm$, and an octahedral tilting ($Cm \rightarrow Cc$) transition has also been found, but the influence of these on elastic/anelastic properties is much more subtle. These additional instabilities do not yield the classical softening response expected from linear/quadratic strain order parameter coupling. Similarly, they are not accompanied by acoustic loss that would signify twin wall mobility. It appears both that the multiple order parameters lock in together in some way that prevents strain relaxation and that the expected adaptive microstructure also does not relax under external loading, at least when measured at frequencies of $\sim 0.1$–1 MHz.

The second dominant feature of the elastic behaviour is precursor softening in a temperature interval of up to $\sim 100$ K above the cubic–tetragonal transition point. The form of softening does not fit descriptions arising from phenomenological models of soft mode dispersion or of relaxor ferroelectrics. It is instead considered in terms of coupling of acoustic phonons with a central peak mode due to local correlations and/or dynamic microstructure.

Finally, concave-up stiffening with falling temperature and reductions in attenuation below $\sim 100$ K appear to be signatures of a material with heterogeneous local strains which have a spectrum of relaxation times. Such heterogeneity must then have a bearing on the magnetoelastic properties when PFN is added in solid solution. Although no direct evidence for significant magnetoelastic coupling has been found, strain heterogeneity may well have some influence both on the magnetic ordering and the development of spin glass.

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Appendix: Formal Strain Analysis

The $\Gamma_4$ order parameter for the $P4mm$ and $Cm$ structures contains three components, with $q_1 = q_2 = 0$, $q_3 \neq 0$ and $q_1 = q_2 \neq q_3 \neq 0$, relaxation times.
respectively. As set out in Carpenter et al. [28], spontaneous strains, \(e\), for the tetragonal structure depend on their variations according to

\[ e_a = e_1 + e_2 + e_3 \propto e_i = \frac{1}{\sqrt{3}} (2e_3 - e_1 - e_2) \propto q_3^2 \]  

(3)

and for the monoclinic structure as

\[ e_a = (e'_1 + e'_2 + e'_3) \propto (2q_1^2 + q_3^2) \]  

(4)

\[ e'_i = \frac{1}{\sqrt{3}} (2e_3 - e_1 - e_2) \propto (q_3^2 - q_1^2) \]  

(5)

\[ e'_o = (e'_1 - e'_2) \propto q_3^2 \]  

(6)

\[ e'_o \propto q_1q_3. \]  

(7)

e_a is the volume strain, \(e'_i\) is the tetragonal shear strain, \(e'_o\) the orthorhombic shear strain and \(e'_o\) a monoclinic shear strain. Reference axes, X, Y and Z, for strains of temperature dependence of \(e'_o\) can be represented by Eq. 8 for both PFN and PZT, consistent with close to tricritical character for the \(P4mm - Cm\) transition if \(e'_o\) scales with the square of the driving order parameter. The trajectory across order parameter space can be represented by the variation with falling temperature of \(e'_o\) and \(e'_3\), arrows indicate the direction of falling temperature.

The variation of \(e'_o\) for the \(P4mm - Cm\) transition can be well represented by

Figure 10  
(a) Strain variations for \(\text{Pb(Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3\) determined from lattice parameters given in Fig. 3 of Noheda et al. [153]. Strain values for PFN are reproduced from Carpenter et al. [28] (note: \(e'_o\) in Appendix Fig. 10 of that work was given with the wrong sign).  
(b) Both \(e'_1\) and \(e'_2\) vary linearly with temperature, consistent with the \(Pm3m - P4mm\) transition being close to tricritical in character.  
(c) Detail from (b) showing that the


\[
\epsilon_3^2 \propto \left( \cosh \left( \frac{\Theta_o}{T_c} \right) - \cosh \left( \frac{\Theta_r}{T} \right) \right),
\]

which is the standard solution to a Landau expansion with saturation temperature, \( \Theta_o \), for the order parameter [154, 155]. If \( \epsilon_3^2 \) scales with the square of the driving order parameter for this transition, the data are also consistent with close to tricritical character; the fit shown in Appendix Fig. 10c has \( T_c = 298 \pm 1 \, \text{K}, \Theta_s = 132 \pm 5 \, \text{K} \). Using components of only one order parameter, as set out for PFN [28], would lead to the expectation of only one instability such that the evolution of (ferroelectric) order parameter components for both the \( P4mm \) and \( Cm \) structures would extrapolate to zero at the same value of \( T_c \). However, the shear strains for Pb\((Zr_{0.52}Ti_{0.48})O_3 \) clearly indicate two instabilities, separated by \( \sim 300 \, \text{K} \) (Appendix Fig. 10b). Data have been added to Fig. 10a, c to show that the tetragonal strain in PFN does not exceed \( \sim 0.003 \), that the magnitudes of displacements associated with \( q_1 \) and \( q_3 \) are likely to both be small and more nearly equal, in contrast with PZT, and that the two instability temperatures are closer together. The overall pattern of evolution is otherwise the same, however.

Observed strain variations of the monoclinic structure are at least qualitatively compatible with the predictions from linear/quadratic strain/order parameter coupling and a single order parameter, for which Eqs. 3–7 were derived. Firstly, the large tetragonal strain (\( \epsilon_1^t \) values up to 3 \%) and small orthorhombic strain (\( \epsilon_3^o \) values up to 0.3 \%) for Pb\((Zr_{0.52}Ti_{0.48})O_3 \) imply that the structural changes associated with \( q_1 \) are small relative to those associated with \( q_3 \), i.e. the dominant ferroelectric displacement is that of the \( P4mm \) structure. Below the \( P4mm-Cm \) transition, \( \epsilon_3^t \) and \( \epsilon_5 \) are at first barely deflected from the trend established in the \( P4mm \) stability field, consistent with Eqs. 4 and 5 if the contribution of \( q_1 \) is small. On the same basis, from Eqs. 6 and 7, it would be expected that \( \epsilon_5 \) should be substantially larger than \( \epsilon_3^o \) and this is as observed (Fig. 10a). \( \epsilon_3^o \) is expected to scale with \( q_1^2 \) and, to reasonable approximation, \( \epsilon_5 \) appears to be determined primarily by \( q_3^2 \).

A plot of \( \epsilon_3^o \) against \( \epsilon_5 \) therefore provides a representation of the trajectory across order parameter space with falling temperature (Fig. 10d). This appears to be simply the successive development of \( P4mm \) (00\( \bar{f}_0 \)) displacements below \( \sim 651 \, \text{K} \) and \( R3m \) (\( \bar{g}_1 \bar{g}_1 \bar{g}_1 \)) displacements below \( \sim 298 \, \text{K} \).

Below \( \sim 200-250 \, \text{K} \), the trend of \( \epsilon_5 \) reverses, so as to decrease with falling temperature, which is most likely due mainly to the contribution from \( q_3 \) in the \( Cm \) and \( Cc \) structures. While \( \epsilon_3^t \) and \( \epsilon_3^o \) are not obviously affected, the volume strain, \( \epsilon_v \), has a small change in trend that would constitute a negative volume strain associated with the \( Cm-Cc \) transition expected in this temperature interval [44, 52, 53]. Based on lattice parameters of Clarke and Glazer [55], the analogous \( R3m-R3c \) transition in Pb\((Zr_{0.9}Ti_{0.1})O_3 \) is also accompanied by a volume strain of \( \sim 0.001 \), without any change in the trend of shear strain arising from the \( Pm\bar{3}m-R3m \) transition. In \((Pb_{0.91}Sr_{0.06})(Zr_{0.55}Ti_{0.45})O_3 \) the \( Cm-Cc \) transition is clearly accompanied by a small, negative volume strain [63].

The focus here is on strain evolution because of its implications for the form of variations of the elastic constants. This treats the average structures without consideration of the possibility that the tetragonal and monoclinic or tetragonal and rhombohedral phases coexist over some temperature interval near the MPB of PZT (e.g. [105, 156, 157]). MPB transitions are also known to be complicated by the possible presence of nanotwinning, as has considered in the context of adaptive structures (e.g. [76, 158]).

The requirement for two critical temperatures follows the view of Souza Filho et al. [159] but is not considered further here. Cordero et al. [106] and Cordero et al. [109] suggested that the second instability could have bilinear coupling between the monoclinic shear strain, \( \epsilon_5 \) and the driving order parameter.
parameter, which is allowed by symmetry for a discrete P4mm–Cm transition with Γ3 of the parent P4mm space group as the active representation. If this were correct, ε′ would be an improper ferroelastic strain occurring by linear/quadratic coupling with the driving order parameter while ε5 would be proper and the expected relationship between them would be ε′ ∝ ε5. This possibility appears to be ruled out by the linear relationship between ε′ and ε5 for both Pb(Zr0.52Ti0.48)O3 and PFN shown in Appendix Fig. 11.

Finally, it is well understood that the boundary between stability fields for R3m and P4mm structures with respect to a Pm3m parent structure can be considered in terms of the changing values of the coefficients for fourth-order terms in the full Landau free energy expansion. The usual expansion can be written in the form (from [160]).

\[
G = \frac{1}{2} a \Theta_{s} \left( \coth \left( \frac{\Theta_{s}}{T} \right) - \coth \left( \frac{\Theta_{s}}{T} \right) \right) (q_{1}^{2} + q_{2}^{2} + q_{3}^{2})
\]

\[
+ \frac{1}{4} b (q_{1}^{2} + q_{2}^{2} + q_{3}^{2})^{2} + \frac{1}{2} b' (q_{1}^{2} + q_{2}^{2} + q_{3}^{2})
\]

\[
+ \frac{1}{6} c (q_{1}^{2} + q_{2}^{2} + q_{3}^{2})^{3} + \frac{1}{6} c' (q_{1} q_{2} q_{3})^{2}
\]

\[
+ \frac{1}{6} c'' (q_{1}^{2} + q_{2}^{2} + q_{3}^{2}) (q_{1}^{4} + q_{2}^{4} + q_{3}^{4}) + \frac{1}{4} \Theta_{s} (q_{1}^{2} + q_{2}^{2} + q_{3}^{2})
\]

\[
+ \frac{1}{6} \left[ \sqrt{3} \Theta_{s} (q_{1}^{2} - q_{2}^{2}) + \Theta_{s} (2 q_{3}^{2} - q_{1}^{2} - q_{2}^{2}) \right]
\]

\[
+ \frac{1}{6} \left[ 3 \Theta_{s}^{2} (q_{1}^{2} q_{2}^{2} + q_{2}^{2} q_{1}^{2} + q_{1}^{2} q_{2}^{2}) + \frac{1}{4} (C_{11} - C_{12}) (C_{11} e_{1}^{2} + e_{2}^{2})
\]

\[
+ \frac{1}{6} (C_{11} + 2 C_{12}) e_{1}^{2} + \frac{1}{2} C_{44} (e_{1}^{2} + e_{2}^{2} + e_{3}^{2}) \right]
\]

(9)

Setting the equilibrium condition, ∂G/∂ε = 0, and substituting for strains gives

\[
G = \frac{1}{2} a \Theta_{s} \left( \coth \left( \frac{\Theta_{s}}{T} \right) - \coth \left( \frac{\Theta_{s}}{T} \right) \right) (q_{1}^{2} + q_{2}^{2} + q_{3}^{2})
\]

\[
+ \frac{1}{4} b (q_{1}^{2} + q_{2}^{2} + q_{3}^{2})^{2} + \frac{1}{2} b' (q_{1}^{2} + q_{2}^{2} + q_{3}^{2})
\]

\[
+ \frac{1}{6} c (q_{1}^{2} + q_{2}^{2} + q_{3}^{2})^{3} + \frac{1}{6} c' (q_{1} q_{2} q_{3})^{2}
\]

\[
+ \frac{1}{6} c'' (q_{1}^{2} + q_{2}^{2} + q_{3}^{2}) (q_{1}^{4} + q_{2}^{4} + q_{3}^{4}) + \frac{1}{4} \Theta_{s} (q_{1}^{2} + q_{2}^{2} + q_{3}^{2})
\]

\[
+ \frac{1}{6} \left[ \sqrt{3} \Theta_{s} (q_{1}^{2} - q_{2}^{2}) + \Theta_{s} (2 q_{3}^{2} - q_{1}^{2} - q_{2}^{2}) \right]
\]

(10)

This is essentially the same as the general 246 potential considered by Vanderbilt and Cohen [75], except that the effects of saturation are included and the higher order terms are grouped slightly differently. The renormalised fourth-order coefficients are

\[
b' = b - \frac{i_{2}^{2}}{C_{20}^{4}} - \frac{2 j_{1}^{2}}{C_{11}^{4}} + \frac{4 j_{2}^{2}}{C_{11}^{4} + 2C_{12}^{4}}
\]

(11)

\[
b'' = b' - \frac{i_{3}^{2}}{C_{20}^{4}} - \frac{12 i_{2}^{2}}{C_{11}^{4} + 2C_{12}^{4}}.
\]

(12)

In this form the condition of Thomas and Muller [161] is that b'' < 0 gives the tetragonal structure as the stable form and b'' > 0 gives the rhombohedral structure as the stable form. With sixth-order terms and following [140, 162], (b'' + b') < 0 and b'' > 0 can give the sequence of stability with falling temperature to be cubic–tetragonal–orthorhombic–rhombohedral. The strain data confirm that in the vicinity of the MPB, at least, the system is close also to the tricritical limit, (b'' + b') = 0, as expected from the known proximity of the tricritical point [14, 15, 19, 73, 106].

According to Cordero et al. [106], the tetragonal–monoclinic transition appears to be reversible at Pb(Zr0.52Ti0.48)O3 but displays a hysteresis between heating and cooling at Pb(Zr0.535Ti0.465)O3 and Pb(Zr0.545Ti0.455)O3. This would place a tricritical point near Pb(Zr0.52Ti0.48)O3 as for the ferroelectric transition, and is consistent with tricritical character implied by the strain analysis. In this case, however, the transition would appear to be first order at Zr-rich compositions and continuous at Ti-rich compositions, which is the reverse of what is observed for the tricritical point of the ferroelectric transition at higher temperatures.

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