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Unravelling the complexity of co-existing phases in piezoelectrics

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Piezoelectric materials are critical for the operation of a vast array of contemporary electronics and devices including sensors, actuators, transducers, capacitors, non-volatile memory devices and they show great promise for energy harvesting. Their performance is dependent on cation displacements that are allowed in non-centrosymmetric structures. Unfortunately, the use of piezoelectric materials is temperature constrained by thermally activated non-centrosymmetric to centrosymmetric phase transitions. This is especially true for the industry standard piezoelectric, $PbTi_{1-x}Zr_xO_3$ (PZT), which is a solid solution between $PbTiO_3$ and $PbZrO_3$. The highest performance in the PZT solid solution falls at the so-called morphotropic phase boundary (MPB) between rhombohedral (*R3m*) and tetragonal (*P4mm*) phases. This region contains a low-symmetry monoclinic structure. Around the MPB, the rhombohedral structure is better described in space group *R3c*.

The complexity of the MPB can be further elaborated by considering the tilting of the corner-sharing octahedra. In the rhombohedral R3c crystal structure, the octahedra have out-of-phase tilting about the pseudocubic [111] direction, described by the Glazer notation $a^-a^-a^-$, and the cations are displaced along the same direction. In the tetragonal P4mm structure there is no tilting $(a^0a^0a^0)$ and the polarization is along [001]. Like the rhombohedral R3c structure, the two intermediate monoclinic structures only contain out-of-phase tilts, in Cm the tilting is modified from $a^-a^-a^-$ to be more like $a^\circ b^-b^-$, whereas in Cc it is more like $a^-a^-c^-$. The polarization in Cm is rotated toward the monoclinic plane (e.g. between [001] and [110]), whereas in Cc it is noncollinear, generally between [001] and [111]. Thus, the superlattice reflections diagnostic of the tilting all involve softening of a phonon mode at the cubic R point. Couple to this the pathological tendency for perovskites to show pseudosymmetry resulting in extensive overlap of reflections, the challenge of identifying the phases present in the MPB is apparent. But wait, there is more to consider. Anisotropic peak broadening emerges across the MPB associated with the phase transitions.

Two of the most pressing goals in the search for new and/or improved piezoelectrics is to reduce, and ultimately eliminate, the amount of Pb and to stabilize the non-centrosymmetric to higher temperatures. The complex ferroelectric ceramic $(1-x)BiFe_{2/8}Ti_{3/8}Mg_{3/8}O_3-xPbTiO_3$ (BFTM-PT) with x = 0.25-0.373 does both but the question is how? Richtik, Manjón-Sanz and Dolgos (2025) address this in current issue of *Acta Crystallographica Section B*. Bi-based perovskites are an obvious target to replace PZT as Bi³⁺ is isoelectronic with Pb²⁺, both containing a stereochemical active $6s^2$ lone pair of electrons. Despite numerous studies, PZT remains the benchmark.

Establishing accurate and precise structures in BFTM-PT ceramics is further complicated considering the relative X-ray and neutron scattering lengths. The presence of the very heavy lead and bismuth cations limits the power of X-ray methods to determine the positions of the oxygen atoms that describe the octahedral tilting, and the negative neutron scattering length of Ti (b = -3.438 fm), often quoted as a strength of neutron scattering, results in very low effective scattering lengths (b = 0.64-1.46 fm) when Ti occupies the same crystallographic site as Fe (9.45 fm) and Mg (5.375 fm). For reference, vanadium, which is often considered to be 'neutron silent', has a scattering length of -0.38 fm. Thus, the polar displacement of the *B*-site cation may be poorly described. The solution adopted by Richtik *et al.* was to refine the structures within their studied BFTM-PT ceramics using combined X-ray and neutron diffraction data, measured at the Canadian Light Source and Spallation Neutron Source, respectively. The structures are refined using *TOPAS*. The synchrotron X-ray diffraction (SXRD) data provide sensi-



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tivity to the distortions of the cell metric and the neutron powder diffraction (NPD) data to the anion displacement.

The strategy used by Richtik et al. is a textbook example of how to address the complex crystallinity in such a multiphase material. First the cell metrics were determined using Pawley fit to combined SXRD and NPD data sets. Given the different counting statistics of the two data sets the first challenge is to appropriately weight the data sets: this was done as the sum of the absolute value of Y_{observed} in the NPD data divided by the sum of the absolute value of Y_{observed} in the SXRD data. This enabled Richtik et al. to establish the phases present across the MPB and, whilst not highlighted in their work, to parameterize the macrostrains responsible for the non-Gaussian peak shape shown in their Figure 4. Following space group determination via Pawley fits, full pattern Rietveld refinements were completed to determine the crystallographic structure of each phase. Since the X-ray scattering power of isoelectronic A-site cations Pb^{2+} and Bi^{3+} are essentially identical and their neutron scattering lengths are very similar (9.49 and 8.64 fm, respectively), they were constrained to occupy the same position in each of the investigated structures. As noted above, a similar constraint was necessary for the *B*-site cation. There is an intriguing change in the relative size of the refined atomic displacement parameters for the A-site cation across the MPB that hints at more complex local structure displacements than can be established by Rietveld analysis. Bond valence sums (BVSs) suggest that the smaller Bi^{3+} cations are underbonded, whereas the larger Pb^{2+} cations are overbonded. In all compositions, the BVS of the Fe³⁺ cation was clustered around 3.0. However, the BVS showed the Ti⁴⁺ cations to be underbonded whereas the Mg² cations

were overbonded. This is consistent with the previous reverse Monte Carlo modelling of neutron scattering data alone, which has revealed that, on the local scale, Ti^{4+} has a distinct environment compared with the Fe³⁺ and Mg²⁺ environments (Chong *et al.*, 2012).

The analysis reveals a subtle minimization in the lattice distortions at the MPB; it is postulated that this coincides with a decrease in the strains between domains facilitating increased domain wall motion, which may be the reason for the enhanced performance at the MPB in BFTM-PT ceramics.

Having established an accurate and precise phase diagram across the MPB in BFTM-PT ceramics, Richtik *et al.* (2025) then seek to correlate this with the important ferroelectric properties of the materials. Rowe *et al.* (2023) established that the piezoelectronic coefficients d_{33} and d_{33}^* were most favourable near x = 0.30; this corresponds to the composition with the highest weight % of the *Cc* phase. Intriguingly there is an unexpected increase in d_{33} (Rowe *et al.*, 2023) at x = 0.375 that Richtik *et al.* show is associated with a change in the monoclinic structure from *Cc* to *Cm* and an increase in the amount of the untitled *P4mm* phase present. Deep understanding of that observation remains the next challenge.

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