Revisiting the structural evolution in powders and single crystals of PMN-xPT

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The intimate connection between electromechanical properties and structure mandates that determination and understanding of the crystal structure is prominently important for interpreting piezoelectric properties. Indeed, it is well-known that the best piezoelectric properties in Pb-based ferroelectric relaxors, such as (1-*x*)$PbMg_{1/3}Nb_{2/3}O_3$-*x*$PbTiO_3$ (PMN-*x*PT), occur at morphotropic phase boundaries (MPBs) that separate different ferroelectric symmetries, in particular pseudorhombohedral and tetragonal symmetries. Nevertheless, the phase diagrams of such systems are complicated by a variety of factors: (i) powder diffraction patterns can be well fit by a number of structures, and the use of a higher or lower symmetry is often a non-trivial choice; (ii) there is a significant amount of local atomic disorder such that the local structure differs from the average structure; (iii) there are discrepancies between single crystal and powder diffraction measurements [1]; (iv) differing line-shapes have been observed from the same crystal depending on the X-ray wavelengths [2]. (iii) and (iv) can be understood as a consequence of a skin effect such that the skin or surface layer of the single crystal possesses a different structure than the bulk interior, though this remains a controversial subject [3]. We have reinvestigated the phase diagram of PMN-*x*PT using powder neutron diffraction on two sets of powders (*x*=0.1, 0.2, 0.3, and 0.4), with one set annealed after grinding to promote oxygen stoichiometry and to relieve grinding-induced strain, in order to determine how such strain might affect the crystal structure and perhaps have led to ambiguity in the phase diagram. Furthermore, we directly compare the profiles of Bragg reflections measured on these powders with measurements of single-crystals.

Briefly, we found that polycrystalline samples of all compositions studied ($0.1 \leq x \leq 0.4$) possess a ferroelectric ground-state. Consistent with the work of Singh *et al.* [4], our refinements favored a monoclinic (s.g. *Cm*) structure on the Ti-poor side of the MPB, though such a conclusion is based on the quality of agreement factors in Rietveld refinements rather than the observation of a splitting not allowed by the rhombohedral (*R3m*) symmetry. Regardless of whether the refinement was carried out in monoclinic or rhombohedral symmetry, a slightly smaller ferroelectric distortion was consistently obtained for the set of samples annealed after grinding to reduce strain and promote oxygen stoichiometry as compared to the as-grown samples. The notion of strained crystals having a larger distortion would be consistent with a skin effect in single crystals, provided that the surface layer of the crystals was significantly more strained than the interior. Nevertheless, the subtlety of this effect in our polycrystalline samples suggests that external, mechanical sources of strain, such as grinding or polishing, are unlikely to account for the differences between powders and single crystals that have been attributed to a skin effect.

Direct comparisons between the observed lineshapes of select Bragg reflections show that our polycrystalline samples are inconsistent with measurements of single crystals on the Ti-poor side of the MPB. We argue that the polycrystalline grains are essentially entirely composed of "skin" and attribute the different lineshapes of single crystals and powders to a skin effect. Interestingly, on the Ti-rich (tetragonal) side of the MPB, we find that the structures of the polycrystalline and single crystal samples

become consistent with one another. The cross-over from a regime where there is a skin-effect to one where the skin-effect disappears occurs around the MPB at a composition $x \leq 0.40$. We have constructed a phase diagram that illustrates the evolution of both polycrystalline and single crystal ground-states. We suggest that the disappearance of the skin effect is related to the relative strengths of the ferroelectric distortion and random electric fields. An expanded discussion can be found in [5].

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