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Structural Complexities of $PbTi_{0.5}Fe_{0.5}O_3$ Nanocrystals Revealed by HRTEM

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Multiferroic materials, i.e. materials that possess more than one ferroic order (ferro- or antiferro-magnetic, ferroelectric, ferroelastic, and so on) are of great current interest because they provide means to combine electronic and magnetic device functions into a single class of materials. One approach, in the search for new materials, has been to substitute Fe into a ferroelectric lattice, like the $PbTiO_3$ perovskite structure, in an attempt to generate multiferroic coupling. Among the many questions, in ongoing efforts to understand multiferroic behavior, is whether multiple ferroic order is a result of the subtle effects of the coexistence of two types of structural phases (not necessarily "chemical" phases) fueling intense structural investigations at the micro- and nano- level. This structural study focuses on $PbTi_{0.5}Fe_{0.5}O_3$ (PTFO), a material reported to display room temperature magnetoelectric behavior[1].

The present HRTEM study is performed using a Hitachi H9000NAR instrument operated at 300keV. It is part of systematic synthesis and multi-technique characterization of $PbTi_{1-x}Fe_xO_3$ (PTFO) in the range $0<x<0.5$. Samples were synthesized using a modified Pechini sol-gel process based on a citric acid–glycerol route, followed by pulverization, calcination, and annealing, yielding nanopowders[2] that were then suspended ultrasonically in methanol and pipetted onto TEM grids covered with ultrathin and/or holey amorphous carbon supporting films. Lead(II) Nitrate, di-hydroxy bis(ammonium lactato) titanium (IV) solution, and Iron(III) nitrate nonahydrate were used as sources of Pb, Ti and Fe ions.

Figure 1 shows a low magnification TEM image, and a corresponding SAD pattern from a collection of particles in the x=0.5 PTFO sample. The particle size is in the 20-50nm range, and the polycrystalline SAD rings, in agreement with the powder X-ray diffraction pattern in Figure 2, can be indexed based on the allowed $PbTiO_3$ reflections[2]. Rietveld refinement of the XRD data, under the single-phase approximation, finds better fit for the orthorhombic *Pmmm* space group than for the tetragonal *P4/mmm* group of pure $PbTiO_3$. The XRD-determined unit cell parameters for the nano PTFO samples are a=0.3943nm, b=0.3929nm and c=0.3998nm (the bulk $PbTiO_3$ parameters are a=b=0.3999nm and c= 0.4143nm)[3].

HRTEM studies were undertaken to look into the structure of individual nanocrystals. Figure 3 shows images of a dominant (a) and a minority (b) phase nanocrystal in <100> type orientations. The minority phase has straight fringes with some lattice spacings that coincide with the majority phase, but also spacings that are unique. This is similar to a rare tetragonal form of $PbTiO_3$ with unit cell parameters of a=b=1.236nm and c=1.4534nm. [3] The contrast of the dominant phase appears complicated. After Fourier filtering (inset in Fig. 4a) and superposition of a regular grid (Fig 4b), it becomes apparent that even the individual nanocrystals are composed of sub-domains. We find that the shift of the lattice fringes between the neighboring domains can be explained via translations of corner sharing octahedra into edge-sharing configurations. A better understanding of structural sub-domains within individual nanocrystals could provide clues to the complex multiferroic properties of these materials.

References:

1. V.R.Palkar and S K Malik, *Solid State Communications* 134 (2005) 783
2. S. Sen et al. *(to be communicated)*
3. Powder Data Files 06-0452 and 42-0004

4. This work was supported by NSF-DMR-0449969, 0509691, RGI, AFOSR

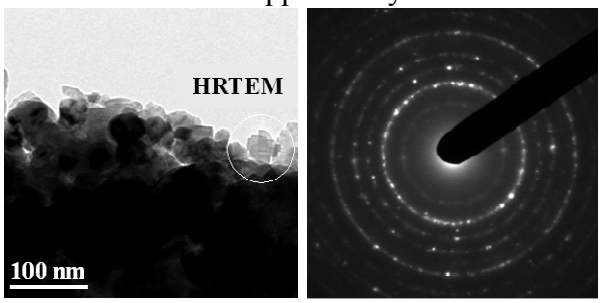

Figure 1: Low magnification TEM image (a), and corresponding SAD pattern (b) of $PbTi_{0.5}Fe_{0.5}O_3$.

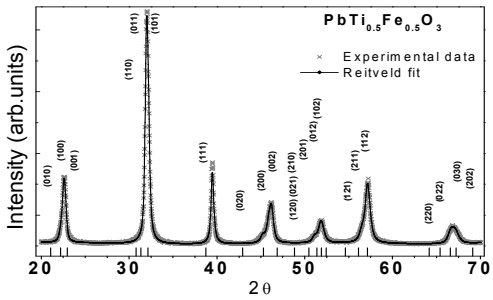

Figure 2: Reitveld refinement (Pmmm symmetry) of X-ray diffraction data of $PbTi_{0.5}Fe_{0.5}O_3$ nanoparticles.

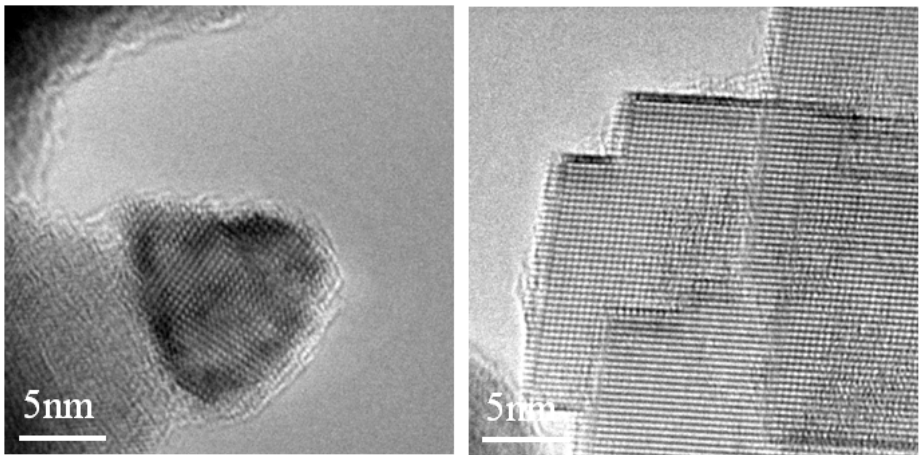

Figure 3: HRTEM images of a dominant (a) and minority (b) phase in <100> type orientations.

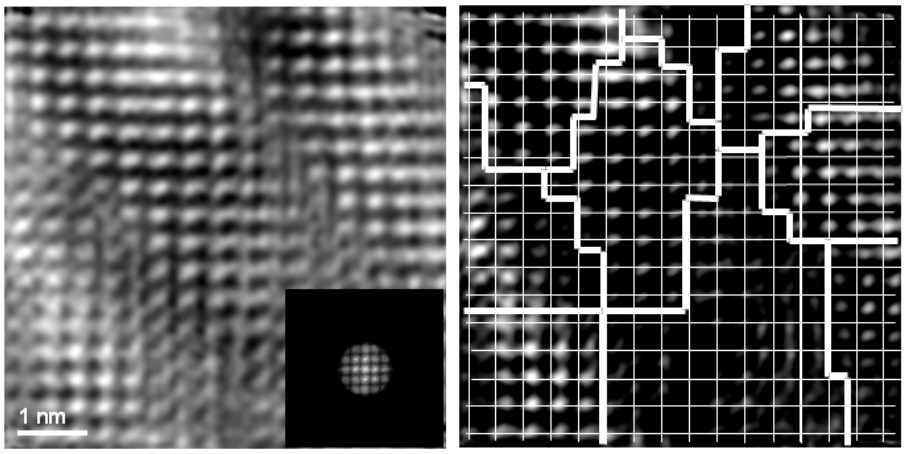

Figure 4: Nano-domains within an individual dominant nanocrystal (a) become more visible after Fourier filtering (inset). (b) The sub-domains in the nanocrystal are marked by white borders.

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