The use electron diffraction and dark field imaging to determine superstructure in perovskites.

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There are 4 mechanisms of superstructure formation in perovskites and related ceramics: i) positional order in stoichiometric compounds; ii) rotations of the O-octahedral sublattice; iii) antiparallel cation displacements and iv) vacancy ordering. Of these 4 mechanisms, positional order is the most researched with extensive studies in the 1980's and 1990's illustrating how order/disorder transitions influence the microwave and ferroelectric properties of compounds such as $Ba(Zn_{1/3}Ta_{2/3})O_3$ and $PbSc_{1/2}Ta_{1/2}O_3$.

Antiparallel or antipolar cation displacements are understood principally because of their ability to generate antiferroelecticity but antipolar displacements are coupled directly to octahedral rotations in perovskites and thus cannot be dealt with independently. Octahedral rotations or tilts were first presented by Glazer in 1972 and 1974 when he described 23 unique ways in which corner-shared octahedra may rotate around the orthogonal axes of the pseudocubic perovskite cell. Most importantly, Glazer recognized that the symmetry of the tilt system mirrored that of the cation distortions. Since this pioneering work, octahedral tilting has been shown to directly influence piezoelectric coefficients and the temperature stability of resonant frequency in perovskites.

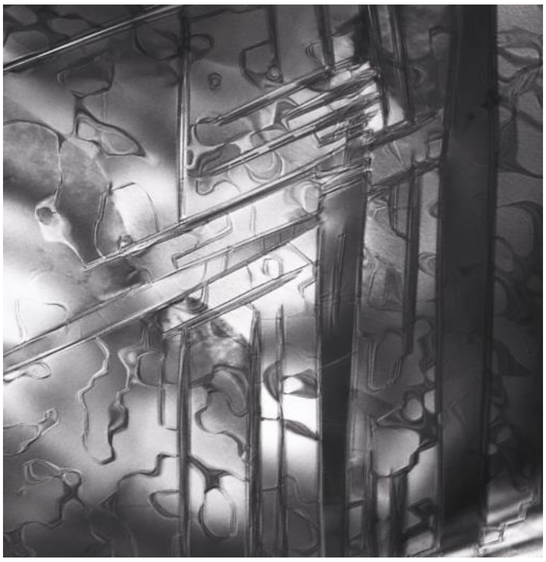

Figure 1. Bright field TEM image illustrating V_{Sr} and O tilt superstructure in rare earth doped $SrTiO_3$

Vacancy order in non-stoichiometric perovskites is poorly understood and rarely shows up in X-ray or neutron diffraction. Vacancies may reside on any of the cation sublattices (Figure 1) of the perovskite structure but their direct influence on properties is largely unknown except for V_O which are often linked with high levels of O-ion and electronic conductivity.

This tutorial reviews the use of Electron Diffraction and Dark Field imaging to determine mechanisms of superstructure formation in perovskite. Particular attention is paid to cases in which there are hierarchical domain structures arising from two or more mechanisms of superstructure formation on cooling from the prototype symmetry.