Do We Understand Why Antiferroelectric Order is Realized in $PbZrO_3$ and $PbHfO_3$?

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In spite of over 60 years of investigations concerning antiferroelectricity in oxidic perovskites ABO_3, it cannot be claimed that we understand the phase transition mechanism(s) leading to this state. Lead zirconate PbZrO3 and lead hafnate $PbHfO_3$ belong to the so called *classical* aniferroelectrics. While the latter has been intensively studied in the last few years, the former one suffered for long time from the lack of systematic investigations. The most important reason was certainly a lack of good quality single crystals and their large enough sizes.

After intense investigations of single crystals of these antiferroelectrics, a hypothesis has been put forward that an antiferroelectric state (order) in ABO_3 perovskites is not realised directly but only through a transient phase of polar (ferroelectric) properties spreading out through a temperature range of few degrees below T_C. It is due to strongly competing zone center and zone boundary instabilities being induced by strong anharmonic lattices. These two instabilities, i.e. softening of the long wave length transverse optic mode of almost displacive type and the accompanying softening of a zone boundary related to transverse acoustic mode are the origin of precursor effects in the form of static (stable) clusters/domains of non-centrosymmetric symmetry. As a result, an anomalous temperature dependence of the elastic stiffness coefficients has been observed before the transition point at T_C [1], and the structure of the paraelectric phase can no longer be considered as a pure paraelectric one [2]. The following results will be presented: the the polarizability model used for calculations, the birefringence in single PbZrO3 and PbHfO3 crystal, structural data, temperature dependencies of dielectric and electromechanical properties, and elastic stiffness coefficients determined by Brillouin spectroscopy.

All the statements above would not have been considered, if earlier investigations on the pre-transitional phenomena in BaTiO3 [3] and $SrTiO_3$ [4] had not been detected. While the stable (static) and non-centrosymmetric (birefringent) microregions were visible above T_C in BaTiO3, which is entirely ferroelectric below T_C, considerably different behaviour was observed in case of $SrTiO_3$, in which precursor effects are related to long wavelength and zone boundary acoustic modes instabilities, and exist even 80K above the transition point at 105K.

References

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