

Materials Science and Technology Division
Materials Theory Group

“Epitaxial strain tunes polarization and band gap in SnTiO₃”

William Parker
Argonne National Laboratory

Friday, June 1, 2012
11:00 a.m.
4100, J-302

Abstract

The existence of a polar SnTiO₃ has been controversial. By stoichiometry and analogy with PbTiO₃, Sn should have a lone electron pair that creates a polar distortion, yet attempts with sintering and pulsed-laser deposition using SnO₂ and TiO₂ precursors have failed to produce a clearly polar SnTiO₃. While several theoretical calculations have examined the properties of a hypothetical perovskite SnTiO₃, two ab initio surveys indicate that the ground state is a non-polar ilmenite structure.

We use first-principles density functional calculations to examine the structural stability of tin titanate polymorphs with SnTiO₃ stoichiometry. We find that the low-energy phases are distorted-perovskite (tetragonal and monoclinic) and ferroelectric-LiNbO₃, all possessing corner-sharing TiO₆ octahedra and polar cation displacements. We show that the monoclinic-distorted perovskite and the ferroelectric-LiNbO₃ phases have locally similar structure, explaining their near-energetic degeneracy.

We also evaluate the relative phase stability of the polar perovskite structures under bi-axial strain. We use the theoretical lattice parameter of cubic perovskite SnTiO₃ to define zero strain and show that the elastic strain energy induced by lattice mismatch with the substrate promotes the stereochemical lone-pair activity and simultaneously enables control over the direction and magnitude of the net electric polarization. The growth-direction-oriented polarization in tetragonal-distorted perovskite transforms to an off-growth-axis polarization in monoclinic-distorted perovskite under tensile strain. In contrast with PbTiO₃, which transitions from out-of-plane polar distortion to an in-plane one under tension, SnTiO₃ retains an out-of-plane polarization under all strains between $\pm 2\%$, strongly attesting to the presence of a lone pair. Mapping the electron localization function confirms the presence of the lone pair on one side of the Sn ions.

Additionally, we find that as the polarization moves away from the growth axis under tensile strain, the SnTiO₃ electronic band gap increases, unlike PbTiO₃ whose gap changes little under tension. We attribute this dependence of the gap on the direction of the polar distortion presents the opportunity to tune it dynamically, through applied electric field or elastic strain, if SnTiO₃ is grown as a thin film close to the phase boundary.

Finally, motivated by the propensity for tin to exist in the 4+ oxidation state, we investigate antisite point defect pairs, namely the substitution of Sn on a Ti site. Simulating, a 12.5% defect density, we show that antisite substitution leads to metallic behavior from the partial occupation of the formerly empty Ti d bands. The metallic screening decreases the repulsion between the Sn²⁺ lone pairs and oxygen atoms and subsequently reduces the magnitude of but does not quench the cooperative polar distortions.

Host: Fernando Reboredo (241-4325, reboredofa@ornl.gov)