Point Defects in (001)-strained $BiFeO_3$

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We study the interplay between point defects and epitaxial strain across the strain-induced isosymmetric phase transition in epitaxial $BiFeO_3$ thin films by density-functional theory (DFT) calculations. The isosymmetric phase transition at 4.5% compressive strain in (001)-oriented $BiFeO_3$ is a prime example of the tremendous success of strain engineering of enhanced properties in epitaxial thin films. Point defect formation during thin film deposition is unavoidable, and defects will impact the material properties. We find that the isosymmetric phase transition is stabilized by Bi vacancies, and implicitly that Bi vacancies are more stable in the tetragonal "T-phase" than in the rhombohedral "R-phase". The band gap is significantly lowered by Bi vacancies, by 1.6eV in the "T-phase", which can also give rise to metallic behavior at low compressive strains. In contrast to the perfect rhombohedral perovskite, where strain has negligible effect on the magnetic behavior, Bi vacancies produces a net magnetic moment of ~1μ_B and ~3μ_B per vacancy for the "T-phase" and "R-phase" respectively. From a structural point of view the out-of-plane rotation of the FeO_6 octahedra disappear upon transforming from the "R-phase" to the "T-phase". The in-plane tilting mode also decreases, making the Glazer tilt pattern $a^-a^-c^+$. Upon introducing a Bi vacancy the in-plane Fe-O bonds are more sensitive to strain, and the octahedral tilting angles are larger in the "T-phase" than the in "R-phase", yielding a $a^-a^-c^-$ tilt pattern. We also analyze Bi-O vacancy pairs with different orientations of the oxygen vacancy with respect to the in-plane and out-of-plane directions. The calculated formation enthalpies of these vacancy pairs show that out-of-plane oxygen vacancies, perpendicular to the (001) stain plane, form more readily in the "T-phase", while in-plane oxygen vacancies, in the strain plane, are more favored in the "R-phase". Finally we address the implications for thin film growth and annealing.