

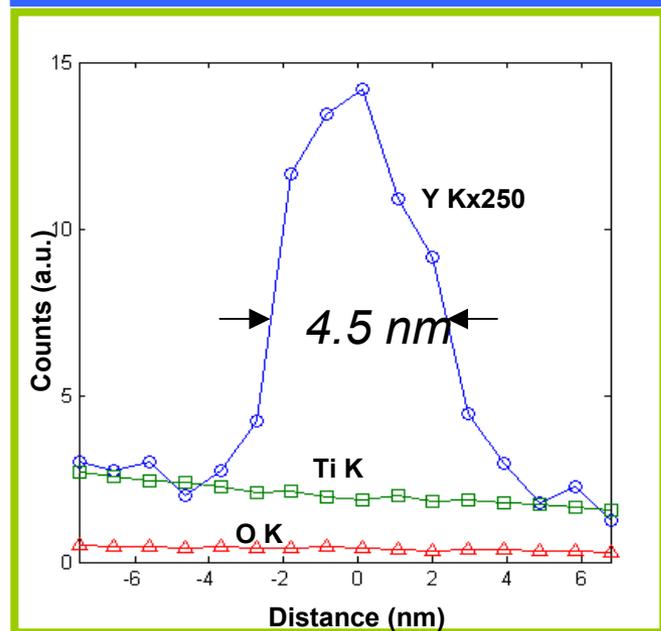
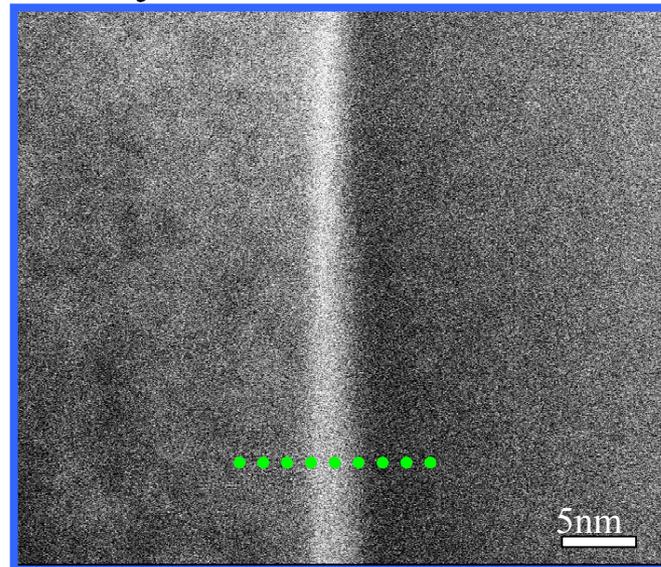
Solute Segregation to TiO₂ Grain Boundaries

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Motivation: Solute and point defect segregation to the grain boundaries in polycrystalline ceramics is an important phenomenon that affects multiple physical properties (e.g. mechanical and electrical). This research focuses on fundamental measurements of grain boundary segregation in TiO₂ and its implications for electrical behavior. The findings will help establish predictive, quantitative models for grain boundary electrical behavior in a wide class of ceramics used in electrical applications.

Results: Segregation of yttrium (Y) to TiO₂ grain boundaries has been confirmed and quantified by analytical transmission electron microscopy. Direct correlations between the grain boundary segregation and electrical barriers and the interfaces have been established.

Images: (top) Z-contrast scanning transmission electron micrograph of a grain boundary in TiO₂. The bright intensity corresponds to Y segregation to the boundary. (bottom) Energy-dispersive x-ray profiles across the boundary confirm the Y segregation and are used for solute segregation quantification.



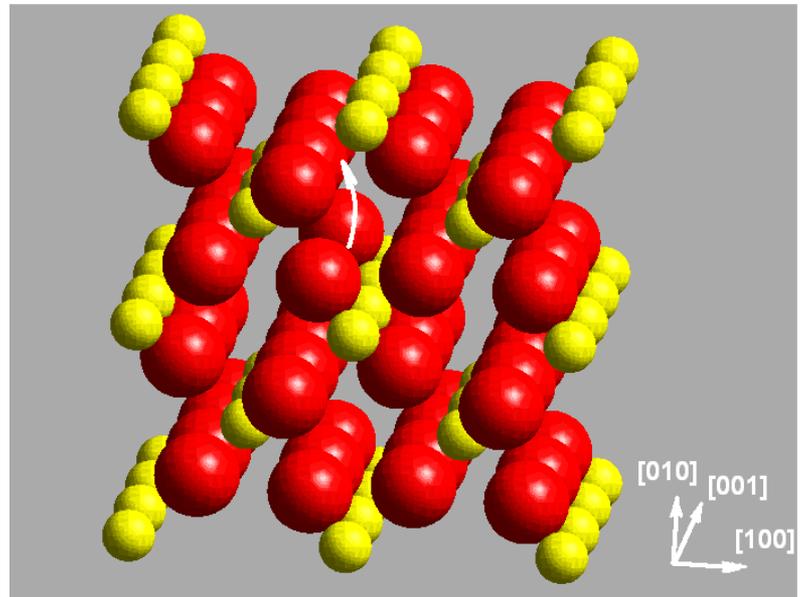
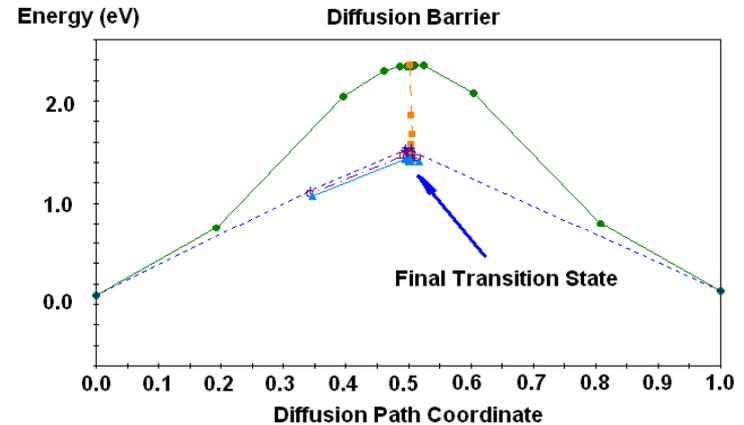
Defect Enthalpies and Diffusion in TiO₂

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Objective Defects such as oxygen vacancies (V_O) and titanium interstitials (Ti_i) play a crucial role in the electrical and photovoltaic behavior of TiO₂. While the diffusion of V_O on the TiO₂ (110) surface has been well studied with STM, its diffusion in bulk rutile is less well understood.

Results Using first-principles calculations, we have found that both V_O and Ti_i prefer to diffuse in an anisotropic manner in bulk rutile. For example, the Ti_i prefer to diffuse along the [001] direction, and the edge of the oxygen octahedral structure (Oh) in rutile is predicted to be the preferred transition state for V_O rather than the center of the Oh structure. This discovery improves our understanding of intrinsic defect diffusion and will assist in the future exploration of extrinsic defect diffusion.

Images Top: calculated diffusion barrier for V_O in bulk TiO₂. Bottom: Ball model illustrating V_O diffusion path in bulk TiO₂. Red spheres are O and yellow spheres are Ti.



Calculation of Defect Formation Enthalpies in TiO_2

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◆ First-principles calculations are used to calculate the defect formation enthalpies (DFEs) in rutile TiO_2 . They indicate that Frenkel defects are more stable than Schottky defects in agreement with experimental results and disagreement with earlier first principles calculations.

◆ By calculating the total energy of different defect configurations, we found that both Frenkel and Schottky defects prefer to cluster together rather than form a distributed structure.

◆ The reference state and partial pressure of oxygen are shown to have a significant effect on the DFEs. This research helps explain why rutile TiO_2 exists as an oxygen deficient oxide.

◆ **Image:** Ball and stick model illustrating a clustered Schottky defect in bulk TiO_2 . The red spheres are O atoms and the yellow spheres are Ti atoms.

