THESIS DEFENSE

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Investigation of TiO_2 Polymorph Selectivity as Influenced by the Amorphous Precursor State

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Abstract: Polymorphism in the titanium dioxide system provides an opportunity for enhancing performance and functionality through targeted synthesis of phases higher in energy than the ground state. Both the anatase and brookite polymorphs are metastable relative to the ground state structure, rutile. These two metastable polymorphs are often sought after due to their affinities for photocatalysis.

The ability to selectively synthesize each of these titanium dioxide polymorphs would prove invaluable in the pursuit of optimizing material properties for photocatalysis. A fundamental understanding of the mechanisms that guide polymorph formation in this system is critical for proficiently directing the formation of metastable structures from amorphous precursors. Elucidating these mechanisms is the goal of the work contained in this dissertation. Removal of oxygen from the amorphous precursor through decreasing the oxygen pressure during synthesis is shown to stabilize anatase at high oxygen pressures (> 5 mTorr), rutile at low oxygen pressures (< 0.1 mTorr), and brookite at intermediate oxygen pressures (0.5 - 1 mTorr). Pair distribution functions measured from the amorphous precursors show that these changes in Ti–O stoichiometry reconfigure the relative arrangements of Ti octahedra into configurations similar to those found in the unit cell structure of the crystalline polymorph they form. These results suggest structural templating in the amorphous phase as a mechanism for preferentially nucleating and growing both stable and metastable polymorphs.

A concept of amorphous precursor engineering for directing the crystallization of titanium dioxide polymorphs is postulated and discussed. This concept demonstrates a wide-ranging potential for synthesis of metastable phases in polymorphic systems where the stabilization of higher energy phases provides a route to superior functionality over their stable counterparts.

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