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Oriented attachment and growth, twinning, polytypism, and formation of metastable phases: Insights from nanocrystalline TiO_2

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Abstract

Atomic-resolution transmission electron micrographs show that nanocrystalline TiO_2 coarsens by oriented attachment and growth under hydrothermal conditions. In addition to forming homogeneous single crystals, attachment at anatase surfaces leads to twinning on {112} and intergrowths on (001) and {001}. Brookite, a polytype of anatase, occurs at some {112} twin surfaces. Alternating two octahedra-wide structural slabs in brookite are shared with the two adjacent anatase twin domains. Because {112} anatase twin interfaces contain one unit cell of brookite, we propose that brookite may nucleate at twin planes and grow at the expense of anatase. Alternatively, anatase-brookite interfaces may form by oriented attachment of primary brookite and anatase {112} crystallites. In this case, three unit cell-wide lamellae of brookite are interpreted as remnants of larger crystals that partly converted to anatase by propagation of the anatase-brookite interface. Which phase is stable is unclear over this particle size range, and products of random thermal fluctuations may be preserved by quenching. Regardless of reaction direction, polytypic interconversion of anatase and brookite essentially involves displacement of Ti (by **c**/4 brookite) into adjacent octahedral sites in one of the pair of two octahedra-wide structural slabs. The results have broad relevance for nucleation and growth models as they suggest that twinning and polytypism in macroscopic crystals can originate at oriented interfaces between primary nanocrystalline particles early in their crystallization history.