Oriented attachment and growth, twinning, polytypism, and formation of metastable phases: Insights from nanocrystalline TiO₂

R. Lee Penn¹ and Jillian F. Banfield¹,²,*

¹Materials Science Program, University of Wisconsin-Madison, Madison, Wisconsin 53706
²Mineralogical Institute, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan

Abstract

Atomic-resolution transmission electron micrographs show that nanocrystalline TiO₂ 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.

Introduction

Mechanisms of phase transformations, reasons for nucleation of materials considered to be metastable phases, origin of twinning, and explanations for the development of polytypic intergrowths are fundamental questions with relevance across all disciplines involving the solid state. Phase stability may depend upon surface energy differences between polymorphs, so that phase relationships and transformation kinetics may be dramatically modified when particles are small (Banfield et al. 1993; Gribb and Banfield 1997; McHale et al. 1997; Zhang and Banfield 1998). Understanding the relationships between crystal size, crystal morphology, and stability is central to determining the primary mechanisms controlling crystallization. Twinning, stacking faults, and polytypic intergrowths observed frequently in natural and synthetic crystals can originate during nucleation and early growth, or can result from phase transitions or deformation. The early crystallization history is crucial to understanding phase stability and development of some microstructures; therefore, theoretical, experimental, and crystallographic analysis of natural and synthetic particles in the <15 nm range is extremely important.

In this paper, we show that a coarsening mechanism involving oriented attachment followed by growth can directly lead to the formation of defects and intergrowths. Oriented attachment occurs when particles join at specific dimensionally similar crystallographic surfaces. Furthermore, we show that twin interfaces that contain structural elements not present in bulk materials may play an important role in the nucleation of new phases. The nanocrystalline TiO₂ system examined here provides some insights into the kinetics of more general processes in finely crystalline materials.

Experimental methods

The research was conducted using anatase and brookite, TiO₂ polymorphs, consisting of octahedrally coordinated Ti⁴⁺ ions. This material is ideal for the study of phase transformation kinetics and the behavior of nanocrystalline materials because it is easy to synthesize, it lacks structural water, and the 4⁺ oxidation state of Ti is stable under most experimental conditions.

Anatase used in this study was synthesized via the sol gel route described elsewhere (Gribb and Banfield 1997; Bischoff 1992). Following synthesis, anatase sols were dialyzed using a Spectra/Por (MWCO = 2000) membrane with deionized water (changed 11 times) to remove the byproducts of synthesis. Prior to dialysis, sols of anatase had not gelled and had low viscosity (similar to that

* E-mail: jill@geology.wisc.edu