

Kinetics study on phase transformation from titania polymorph brookite to rutile

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Abstract

TiO₂ is a polymorphic material of great scientific interest due to its semiconductor properties and uses in heterogeneous photocatalysis. Understanding the stability of the polymorphs is important for designing TiO₂-based photocatalysts and solar cells. Although the phase transformation of anatase → rutile has been well studied, there is only one published work on brookite → rutile to date. The brookite → rutile transformation has been studied in this work using natural material from the Magnet Cove igneous complex mechanically processed to several micrometers in size. The pure phase brookite is annealed from 800 to 900 °C without detection of the anatase polymorph. The transformation kinetics are described by both the standard first-order model, with an activation energy of $E_a = 411.91$ kJ/mol, and the Johnson–Mehl–Avrami–Kolmogorov (JMAK) model, with an activation energy of $E_a = 492.13$ kJ/mol. The rate parameter of the first-order model for the phase transformation is expressed as $k = 6.85 \times 10^{14} \exp(-49,451/T) \text{ s}^{-1}$ for the first-order model and $k = 4.19 \times 10^{18} \exp(-59,189/T) \text{ s}^{-1}$ using the JMAK model. The obtained activation energy is higher than that of brookite nano-crystals. Our results show that the JMAK model fits the kinetics data better than other models.

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1. Introduction

Crystals of TiO₂ polymorphs are oxide semiconductors that are both physically and chemically stable. The TiO₂ crystals can be used as heterogeneous photocatalysts that can use light energy to drive reactions like photocatalytic production of hydrogen from water and oxidation of organic compounds in air and water [1–5]. TiO₂ micro-crystals and nano-crystals are also used in dye-sensitized solar cells [1,6–8]. Because rutile is the most thermodynamically stable polymorph, it is necessary to understand the kinetics of phase transformations from other polymorphs into rutile. In nature, TiO₂ occurs as a common accessory mineral in igneous and metamorphic rocks and beach sands. The four polymorphs of TiO₂ that are stable on Earth are rutile (tetragonal), anatase (tetragonal), brookite (orthorhombic) and the high-pressure phase TiO₂ (II) with

α -type PbO₂ structure [9]. Brookite is formed by zig-zag chains of octahedra that share four edges. Rutile is formed by zig-zag chains of octahedra that share two edges. Viewed on (010), the brookite octahedra alternately point toward positive or negative *c*-axis. Rutile is formed by edge sharing octahedra along [001] with corner sharing along [110] and [1 $\bar{1}$ 0]. The octahedral chains are rotated at 90° in rutile and nearly 90° in brookite but are not rotated to a large degree in the anatase structure. Rutile is the most thermodynamically stable form while anatase and brookite are metastable and are thought to occur at low temperatures and pressures. The phase stability field of brookite remains undefined. Phase transformation of anatase and brookite to rutile is reconstructive and proceeds directly without involvement of the other metastable phase. The anatase → rutile phase transformation has been studied by numerous investigators [10–13]. Zhang and Banfield [14] have summarized the previous work on anatase-to-rutile kinetics and proposed a modified kinetics model that considers size dependence and interface nucleation factors

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on the reaction rate. To date, only one study of brookite \rightarrow rutile has been published and used monodispersed synthetic nano-crystals [15].

This study uses pure phase natural material obtained from Magnet Cove, Arkansas. The Magnet Cove Igneous Complex is a 94 million years old (Ma) [16] calc-alkaline igneous intrusion into folded Paleozoic sedimentary rocks. Erickson and Blade [20] describe the general geology and interpret the ring-like structure and complex igneous bodies as the eroded roots of a collapsed caldera. The mid-Cretaceous igneous activity in Arkansas follows a southeast to northeast trend possibly caused by the passage of North America over the Bermuda hotspot [16,17]. Fluids derived from late-stage carbonatites-carried titanium, niobium and molybdenum which mineralized the country rocks [18,19]. The titanium was complexed as $K_2TiF_6 \cdot H_2O$ or $Na_2TiF_6 \cdot H_2O$ and transported as a vapor phase derived from carbonatite magmas [18]. Apatite occurs in the igneous complex as the dominant F mineral phase. Rutile mineralization is associated with taeniolite which contains up to 8% F. Brookite mineralization occurred later without fluorine mineral phases [18]. The titanium in final stage fluids formed brookite on quartz aggregates within the folded and fractured novaculite [19]. Veins of brookite-quartz aggregates occur in the lower division of the novaculite, the source of the recrystallized silica. The clay mineralization occurred in altered shale seams in the novaculite [18,20].

Three main economic areas are defined in the complex: the Magnet Cove Co. rutile deposit, the Hardy–Walsh prospect and the Christy deposit. The latter two are both located in the folded layers of Arkansas novaculite. The Christy deposit is located on the east side of Magnet Cove one mile south of the Hardy–Walsh. Brookite occurs within quartz-brookite aggregate vein material and in remineralized novaculite.

2. Experimental method

The brookite for this work was obtained from a specimen of Magnet Cove material. The specimen displays euhedral brookite and quartz crystals in red clay. Brookite occurs as orthorhombic dipyrramids from 2 to 10 mm in size with vicinal planes on $\{100\}$ and well developed $\{112\}$ (Fig. 1). Several 2–3 mm crystals were removed, cleaned and then mechanically processed to a powder with an average size of several micrometers. The source of our sample was likely vein material within the novaculite from the Christy deposit or one of the Hwy 270 outcrops known to produce large brookite crystals [18]. The average composition of the brookite is $(Ti_{0.966}, Nb_{0.016}, Fe_{0.01}, V_{0.008}) O_2$ [19].

Natural brookite and rutile paramorph brookite material were verified as pure phases using X-ray diffraction (XRD) (Fig. 2). X-ray characterization was done on a Scintag Pad V Diffractometer with $CuK\alpha$ radiation. The samples were prepared as a film on a low background

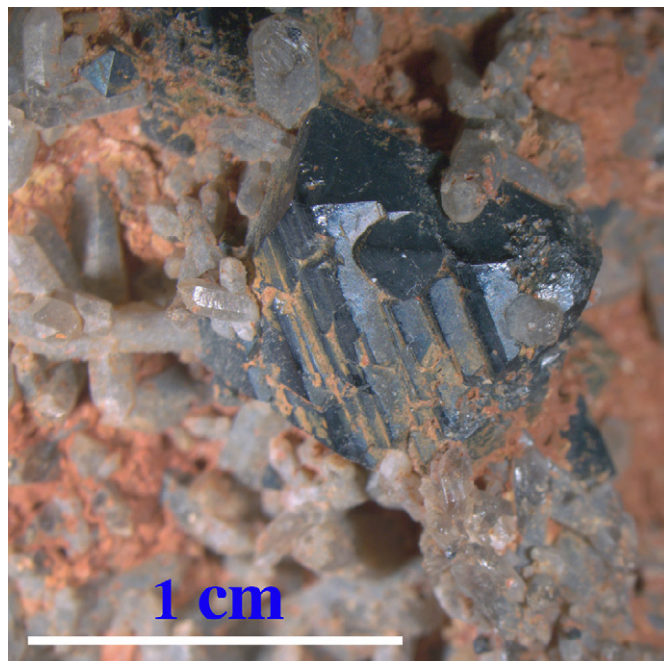


Fig. 1. Photo showing euhedral black brookite crystals and associated minerals of white quartz and red clays.

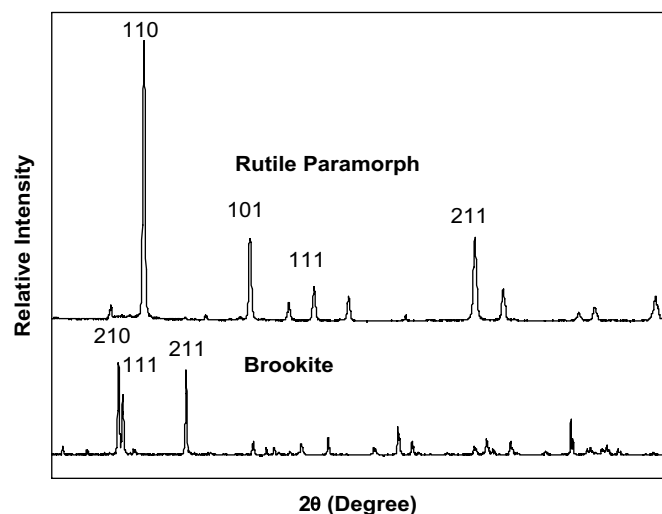


Fig. 2. Diffraction data for pure phase brookite and rutile paramorph specimens from Magnet Cove, AR.

quartz sample holder used to obtain higher-quality patterns. Scan parameters used are 2θ angle $20\text{--}70^\circ$, step size 0.02° and dwelling time of 2 s. Samples consisting of 0.05 g brookite were annealed between 800 and 900 °C up to 40 h. XRD patterns obtained from annealed samples were used for the calculation of weight fraction of the two phases (Figs. 3–5).

Rietveld refinement method was then used to determine the weight fraction of rutile and brookite in the annealed samples. The Rietveld method uses a least-squares approach to refine a theoretical line profile until it matches the experimental profile obtained by standard powder

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