



## Heat capacity and thermodynamic functions of TiO<sub>2</sub>(B) nanowires

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### ABSTRACT

Heat capacities of TiO<sub>2</sub>(B), 50 nm in diameter and several micrometers in length, containing given amounts of anatase were measured using a Quantum Design Physical Property Measurement System (PPMS) over a temperature range from 1.9 to 302 K. After eliminating the contribution from anatase, the heat capacities for TiO<sub>2</sub>(B) were fitted to a theoretical model in the low temperature range ( $T < 9$  K), orthogonal polynomials in the middle temperature range ( $9 < T < 65$  K), and a combination of Debye and Einstein functions in the high temperature range ( $T > 65$  K). The standard molar heat capacity, molar entropy, and molar enthalpy for TiO<sub>2</sub>(B) at  $T = 298.15$  K were determined to be  $(58.18 \pm 0.81)$  J·K<sup>-1</sup>·mol<sup>-1</sup>,  $(52.31 \pm 0.69)$  J·K<sup>-1</sup>·mol<sup>-1</sup>, and  $(9.03 \pm 0.12)$  kJ·mol<sup>-1</sup>, respectively, leading to a Gibbs free energy of  $-(6.56 \pm 0.09)$  kJ·mol<sup>-1</sup>. The heat capacity of TiO<sub>2</sub>(B) is found to be similar to brookite, but significantly higher than those of anatase and rutile when temperature is above 200 K.

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### 1. Introduction

Among all minerals and inorganic compounds, TiO<sub>2</sub> is the few that adopts at least 8 structures such as rutile, anatase, brookite, TiO<sub>2</sub>(B), hollandite, columbite, baddeleyite, cotunnite, and so on [1–3]. There are four naturally occurring TiO<sub>2</sub> polymorphs [4–9], including rutile, anatase, brookite, and TiO<sub>2</sub>(B), with distinct structural parameters as listed in Table 1. These four TiO<sub>2</sub> polymorphs occur as accessory minerals in sediments, metamorphic, and mantle and crustal plutonic and volcanic rocks. Rutile is a common accessory mineral in a wide variety of crustal and mantle-derived rocks. During the prograde metamorphism process, anatase, brookite and TiO<sub>2</sub>(B) could convert to rutile. Coexistence of polymorphs has been reported. For example, TiO<sub>2</sub>(B) forms lamellae in anatase from hydrothermal veins. Anatase, brookite and rutile coexist in metapelites, while anatase, brookite and rutile found together in quartz veins [10–12]. Even though many researches about these four TiO<sub>2</sub> polymorphs in minerals have been done, the reason for the formation of the metastable polymorphs anatase, brookite and TiO<sub>2</sub>(B) in nature are poorly understood. As the research further develops, the thermodynamic properties of these metastable polymorphs have been concerned for further understanding the natural formation.

For instance, Boerio-Goates et al. studied the thermodynamic parameters of anatase and rutile in a temperature range from 30 to 301 K [13], which concludes that the bare small particle specific heats are the same as those of the bulk. Smith et al. determined the thermodynamic parameters as well as phase stability of anatase and rutile in the temperature range from 0.5 to 380 K [14], which indicates that the standard molar Gibbs free energy of transition from anatase to rutile is  $-1.87$  kJ/mol at 298.15 K. Recently, Che et al. investigated the thermodynamic parameters of brookite from 2 to 302 K [15], which has led to the conclusion that the thermal stability of the TiO<sub>2</sub> polymorphs follows anatase < rutile < brookite at 298.15 K. Despite of these great progress, the heat capacity and standard thermodynamic functions of TiO<sub>2</sub>(B) are highly needed for mapping the thermodynamic properties of TiO<sub>2</sub> metastable polymorphs. It is well known that heat capacity has a strong relationship with the crystal structure, being a sum of lattice vibrations, electronic states, and magnetic properties [16]. TiO<sub>2</sub>(B) crystallizes in a monoclinic phase (space group, C2/m), strikingly differing from the orthorhombic phase for brookite (space group, Pbc<sub>2</sub>), tetragonal phase for rutile (space group, P42/mmm), and anatase (space group, I41/amd) [17–20]. Moreover, both vertex sharing and edge sharing occur along the c direction, while TiO<sub>6</sub> octahedra share edges along a and b directions. Among the six Ti–O bonds in TiO<sub>6</sub> octahedra, there exist five different categories. Comparing to other three polymorphs, TiO<sub>2</sub>(B) shows a similar connection pattern on TiO<sub>6</sub> octahedras and categories of Ti–O bonds with brookite, which is distinctly different from anatase

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**Table 1**  
Lattice data for four naturally occurring TiO<sub>2</sub> polymorph structures.<sup>a</sup>

Structure	Space group	Density(g/cm <sup>3</sup> )	Crystal system	Unit-cell data
TiO <sub>2</sub> (B)	C2/m	3.75	monoclinic	a = 1.216 nm, b = 0.374 nm, c = 0.651 nm, β=107.29°
Brookite	Pbca	4.13	orthorhombic	a = 0.917 nm, b = 0.546 nm, c = 0.514 nm
Rutile	P42/mnm	4.25	tetragonal	a = b = 0.459 nm, c = 0.296 nm
Anatase	I41/amd	3.89	tetragonal	a = b = 0.379 nm, c = 0.951 nm

<sup>a</sup> Data of Rutile and Anatase are published by Cromer and Herrington (1955) [17]. Data of Brookite and TiO<sub>2</sub>(B) are studied by Baur (1961) [18] and Marchand et al. (1980) [20], respectively.

and rutile. These structural features would result in similar heat capacities and thermodynamic functions between TiO<sub>2</sub>(B) and brookite, but highly different the thermodynamic properties from anatase and rutile phase as reported elsewhere [15].

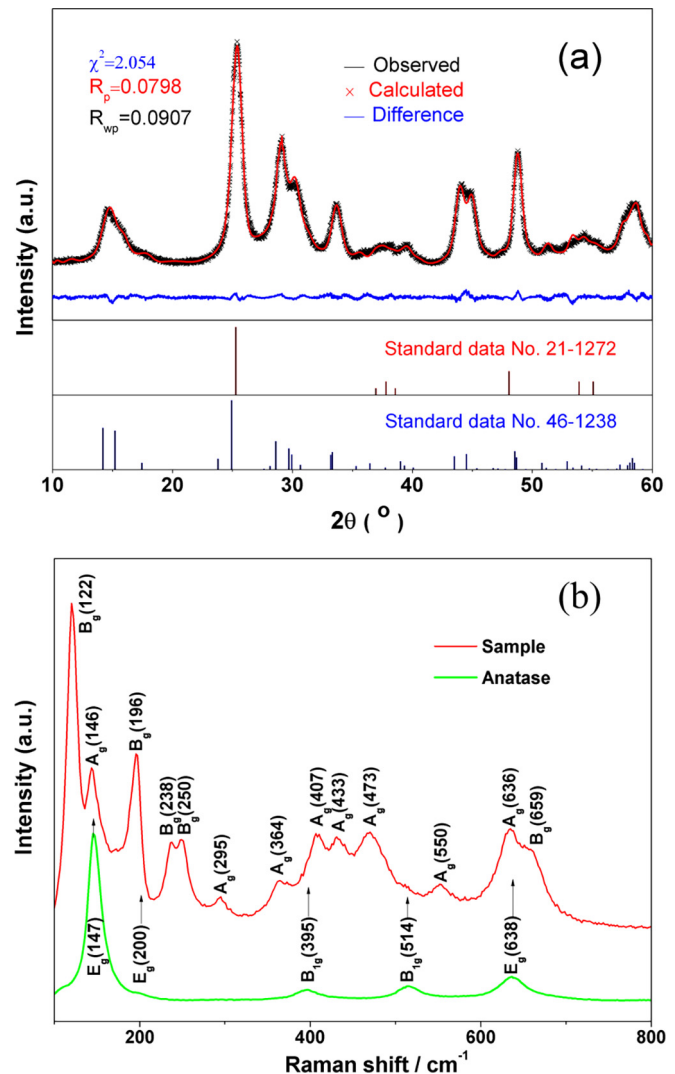
To confirm our assumption, we initiated a study on the heat capacities and thermodynamic functions of TiO<sub>2</sub>(B). The microstructures of TiO<sub>2</sub>(B) were characterized via X-ray, Raman spectrum, X-ray photoelectron spectroscopy, scanning electron microscopy, and transmission electron microscopy. The heat capacities were measured using a Quantum Design Physical Property Measurement System (PPMS) over a temperature range from  $T = 1.9$  to 300 K, and the standard thermodynamic functions have been calculated based on the data fit of the heat capacities which eliminates the contributions of impurity anatase. Comparing to other three common TiO<sub>2</sub> polymorphs, TiO<sub>2</sub>(B) shows a similar heat capacity to brookite TiO<sub>2</sub> phase, but significantly higher than anatase and rutile TiO<sub>2</sub> phases when the temperature is higher than 200 K. The possible reasons have been provided for this interesting phenomenon based on crystal structure and lattice vibration mode analyses.

## 2. Experimental section

### 2.1. Sample preparation and characterization

TiO<sub>2</sub>(B) nanowires were prepared by a hydrothermal method. The preparation procedure could be described as follows: 1 g TiO<sub>2</sub> (P25) was first added into 30 mL of a mixed solution of 10 M NaOH with ethanol at 1:1 volume ratio. After stirring for 1 h, the resulting suspension was transferred into a Teflon-lined stainless-steel autoclave. The autoclave was maintained at 180 °C for 18 h and then cooled to room temperature naturally. The resulting products were filtered, washed with 0.1 M HCl solution that removes residual Na ions, and with deionized water to pH 7, and finally heated at 400 °C for 4 h in air.

Particle composition and purity were analyzed using a Perkin–Elmer inductively coupled plasma atomic emission spectrometer (ICP–AES). Na was detectable by ICP with a concentrations of only 0.167 wt% which could be neglected. Phase purity of the product was measured with powder X-ray diffraction (XRD) at room temperature (see Fig. 1a). It is obvious that the diffractogram confirms the presence of TiO<sub>2</sub>(B) which is monoclinic, a metastable polymorph of TiO<sub>2</sub> (space group C2/m, JCPD No 46-1238). However, it also shows the presence of a small quantity of anatase as represented by the diffraction peaks at two theta of 38.7°, 53.9°, and 55.5°. Raman spectrum is also introduced here to further confirm the presence of anatase. Fig. 1b shows the comparison of TiO<sub>2</sub>(B) sample and anatase which was also synthesized by a hydrothermal method. It is obvious that the spectrum of TiO<sub>2</sub>(B) sample contains two peaks around 395 and 514 cm<sup>-1</sup>, which are attributed to B<sub>1g</sub>(395) and B<sub>1g</sub>(514) of anatase [21,22]. The phase composition was further indicated via the Rietveld refinement method using the general structure analysis system (GSAS) program (see Fig. 1a), which gave the percent content of 88% TiO<sub>2</sub>(B) and



**Fig. 1.** (a) XRD refinement data of the as-prepared sample based on the monoclinic lattice geometry of the space group C2/m (TiO<sub>2</sub>(B)) and tetragonal lattice geometry of the space group I41/amd (anatase), and (b) Raman spectrum of TiO<sub>2</sub>(B) sample and reference anatase TiO<sub>2</sub> [21,22].

12% anatase. Therefore, the stoichiometries of the prepared sample is TiO<sub>2</sub>(B)-0.136 anatase.

XPS is further performed to examine the chemical states of the elements in TiO<sub>2</sub>(B), as shown in Fig. 2. There exists a weak peak at a binding energy around 1073 eV, which could be assigned to Na 1s [23], consistent with our result of ICP. In Fig. 2b, one can see strong XPS signals at 464.05 and 458.34 eV for TiO<sub>2</sub>(B), which can be assigned to the characteristic Ti 2p<sub>1/2</sub> and Ti 2p<sub>3/2</sub> peaks of Ti<sup>4+</sup> species, respectively [24–27]. Splitting Δ-value is 5.71 eV between Ti<sup>4+</sup> 2p<sub>1/2</sub> and Ti<sup>4+</sup> 2p<sub>3/2</sub>, which agrees well with the theoretical

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