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Compression behavior of nanocrystalline anatase TiO_2

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Abstract

We present a synchrotron X-ray diffraction study of pressure-induced changes in nanocrystalline anatase (with a crystallite size of 30–40 nm) to 35 GPa. The nanoanatase was observed to a pressure above 20 GPa. Direct transformation to the baddeleyite-TiO_2 polymorph was seen at 18 GPa. A fit of the pressure versus volume data to a Birch–Murnaghan equation yielded the following parameters: zero-pressure volume, $V_0 = 136.15$ Å^3, bulk modulus, $K_T = 243(3)$ GPa, and the pressure derivative of bulk modulus, $K' = 4$ (fixed). The bulk modulus value obtained for the nanocrystalline anatase is about 35% larger than that of the macrocrystalline counterpart.

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1. Introduction

TiO_2 in the macrocrystalline and nanocrystalline forms is an important material with several known and potential industrial applications. Among the major technological applications of this material are in the pigments, plastics, cosmetics, electronics, and catalysts industries. TiO_2 has also served mineral physicists as a model system in the study of pressure-induced structural phase transitions of oxides relevant to the Earth's mantle, in particular that of SiO_2 [1]. More recently, nanocrystalline TiO_2 has been used as a model system to investigate the size-dependent phase transition behavior of nanoscale oxides in terrestrial environments [2]. Because of the technological and fundamental importance, numerous experimental and computational studies have investigated the phase stability and properties of macrocrystalline TiO_2 polymorphs. Significant progress has been made recently in the identification of various macrocrystalline polymorphs and their properties [3–5]. Only a beginning has been made, however, in the study of the properties and phase stability of nanocrystalline TiO_2 polymorphs. Some experimental studies have recently examined the phase transition behavior of nanocrystalline rutile and anatase ([6–9], also see Ref. [2]). In the case of nanocrystalline anatase, different studies have reported contradictory high-pressure behavior [6,8,9]. In view of the contrasting published data, we undertook a powder X-ray diffraction study of the room-temperature compression behavior of nanocrystalline anatase to 35 GPa with the diamond-anvil cell (DAC) technique and synchrotron radiation.

Previous investigations of pressure-induced transformations in nanocrystalline anatase include that by Liao et al. [6] and Wang and coworkers [8,9]. Liao et al. [6] conducted a high-pressure/low-temperature sintering study of an

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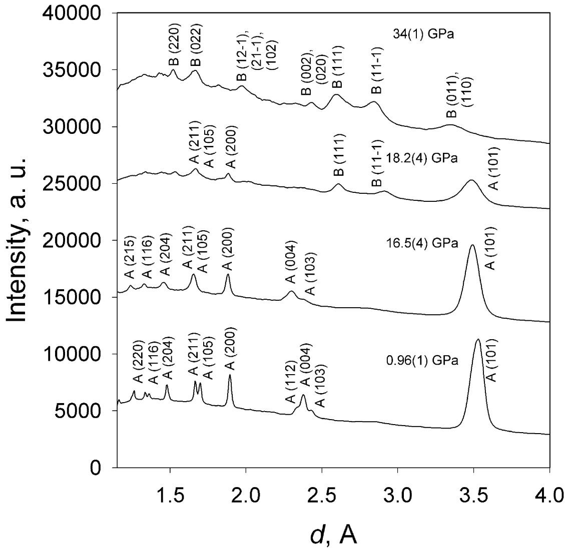

Fig. 1. Representative powder X-ray diffraction patterns obtained from compressed nanocrystalline anatase. Reflections marked A originate from anatase, and those marked B from baddeleyite-TiO_2.

anatase–rutile mixture (in the weight ratio 96:4) with an average crystallite size of about 38 nm in a toroidal-type high-pressure apparatus. They reported that depending on the pressure/temperature combination, the material transformed either to rutile or to srilankite-structured phase (commonly referred to as α-PbO_2-structure or TiO_2-II). The transformation to the α-PbO_2 phase was reported at pressures greater than 4.75 GPa and temperatures as low as 250 °C. At temperatures below about 150 °C, they did not observe formation of rutile at the expense of anatase up to 8 GPa. The grain size of the transformed rutile was found to decrease with sintering pressure, owing to increasing nucleation rate and decreasing growth rate with high-pressure.

Wang and Saxena [8] in a room-temperature DAC study of Raman scattering from nanocrystalline anatase (with crystallite size ranging from 7 to 11 nm) observed that the nanoanatase was stable up to 24 GPa, and then turned to an amorphous phase on further compression in the pressure range of 24–37 GPa. The amorphous material was quenchable to ambient pressure. Subsequently, Wang et al. [9] conducted a high-pressure DAC X-ray diffraction study on a rutile–anatase mixture (of unknown phase ratio) with particle size of 30 nm to about 35 GPa. They observed the appearance of diffraction peaks due to baddeleyite-structured TiO_2 at 8.7 GPa. At about 16.4 GPa, all the rutile and anatase peaks disappeared completely from the X-ray diffraction spectra and only baddeleyite-TiO_2 peaks remained. They noted the presence of strong background in the high-pressure X-ray diffraction spectra, and on the basis of their earlier Raman study [8], attributed this to amorphization of the 30 nm-sized anatase crystallites at a pressure of about 16.4 GPa.

Our X-ray diffraction study is motivated by the need to examine phase-pure nanocrystalline anatase to unambiguously characterize its high-pressure behavior. This will help understand the size-effect on the compression behavior as well as provide a value for the bulk modulus of this material.

2. Experiment

The nanocrystalline anatase used in the experiment was obtained from Altair Nanomaterials Inc.[1] The sample consists of phase-pure (>99.5%) equiaxial crystallites of anatase ranging in size from 30 to 40 nm, as determined by BET, Scherrer, and transmission electron microscopy methods.

Powder X-ray diffraction data were collected from the nanocrystalline sample at the BM01 and ID22 beamlines of the European Synchrotron Radiation Facility (ESRF) Grenoble, France. At the BM01 beamline, the data were obtained with the MAR345 detector using an X-ray beam of wavelength 0.6996 Å and size of 20 × 20 μm, and at ID22, we used a CCD area detector and a highly focused beam of 0.6200 Å wavelength and 2 × 5 μm size. The detector-to-sample distance varied in different experiments from 60 mm (at ID22) to 350 mm (at BM01). Diamonds with culets of 250 or 300 μm were mounted on the seats with 30° opening allowing us to collect the diffraction data to 0.9 Å. Gaskets were made out of a 250 μm thick Re sheet that was pre-indented to 30–33 μm thickness. Holes of 80–100 μm diameter were drilled in the gasket, centered on the indentation. The sample was packed into the hole and the gasket compressed between the opposing diamonds. The diffraction images obtained were integrated using the FIT2D program [10] in order to obtain conventional diffraction spectra. Full-profile refinements of the powder X-ray diffraction data were carried out using the GSAS package [11]. We used Au (99.99%) wire, placed near the center of the pressure chamber, as the internal pressure standard. At 35 GPa, the pressure variation in the center of the sample (within the size of the X-ray beam) was less than 1 GPa.

3. Results and discussion

At ambient pressure and temperature, the nanocrystalline anatase gave the following unit cell constants: $a = 3.7830(3)$ Å and $c = 9.513(9)$ Å, close to the values observed for bulk material ($a = 3.785$ Å and $c = 9.513$ Å: JCPDS file 21-1272).

We collected X-ray diffraction spectra in the pressure range between 0 and 35 GPa at intervals of about 2 GPa to analyze the pressure-induced changes in nanocrystalline anatase and to retrieve an isothermal (room-temperature)

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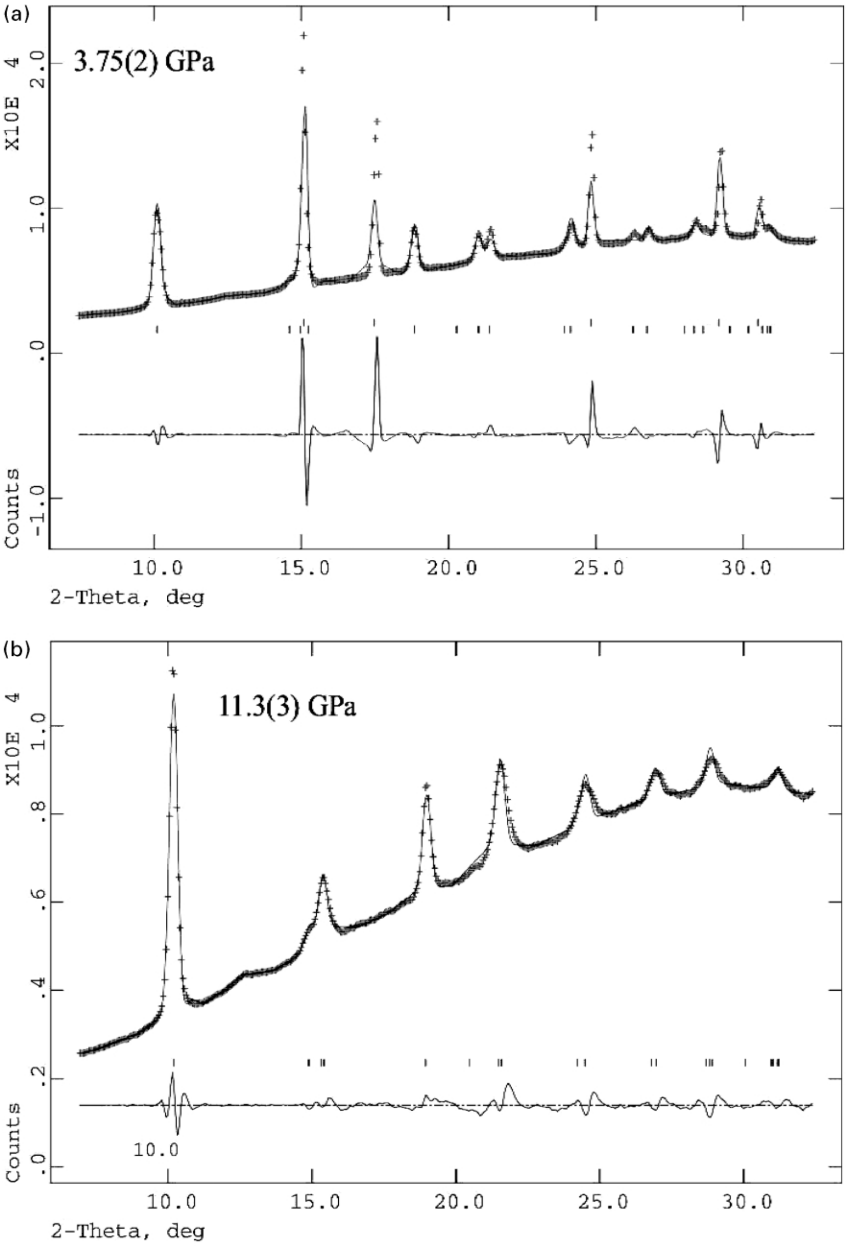

Fig. 2. Examples of the full-profile refinement of the X-ray diffraction data collected: (a) at 3.75(2) GPa and (b) at 11.3(3) GPa. The upper ticks represent Au, and the lower ticks—anatase. Deviation of the refined intensities from those experimentally observed for gold diffraction lines at 3.75 GPa are related to the complex preferred orientation on gold wire.

bulk modulus. A selection of X-ray diffraction spectra representing the entire pressure range is shown in Fig. 1. Fig. 2 shows examples of the full-profile refinement of the diffraction data obtained at two pressures. The diffraction spectrum obtained at 18.2(4) GPa showed, in addition to the anatase peaks, first appearance of the most intense reflections belonging to the baddeleyite-structured TiO_2 (reflections marked as B in Fig. 1). Distinct reflections due to anatase could be seen in spectra obtained up to 25 GPa. We did not observe any diffusion halo or significant increase in the background that can be attributed to amorphization in any of the high-pressure diffraction spectra. As mentioned earlier, Wang et al. [8,9] reported evidence of amorphization above 24 GPa in a phase-pure 7–11 nm sized anatase crystallites and also in a 30 nm-sized anatase/rutile crystallite mixture at 16.4 GPa.

Size-effect on the pressure-induced phase transition of anatase at room-temperature is now rather clear. Single

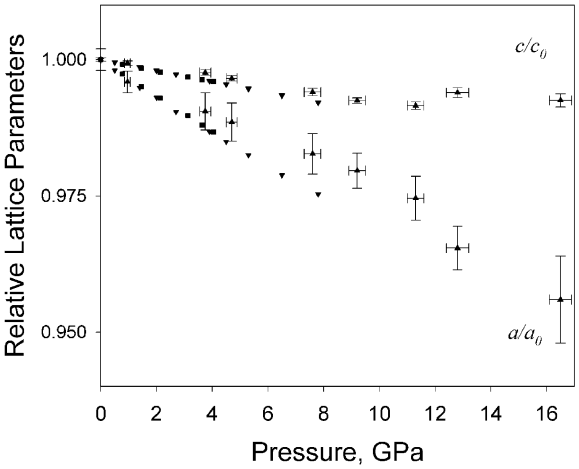

Fig. 3. Variation of relative lattice parameters (a/a_0 and c/c_0) of nano-anatase with pressure (triangles) in comparison with data for polycrystalline bulk material (inverted triangles, from Ref. [18]) and for a single crystal (squares, from Ref. [15]).

crystal anatase transforms to the α-PbO_2-structure at 2.5–7 GPa [13–15]. Although there have been reports of a phase transition in microparticle (polycrystalline) anatase around this pressure [15,16], a recent study seems to suggest that phase transition is suppressed in microparticle anatase to about 13 GPa, where it transforms to the baddeleyite structure [14]. Further increase in stability against pressure is observed for nanocrystalline anatase. The data from this study as well as from the work of Wang and coworkers [8,9] demonstrate that smaller the crystallite size of the nanocrystalline anatase, larger the transition pressure. We observed the preservation of single-phase nanocrystalline anatase to about 16.5 GPa at room-temperature, and its coexistence with baddeleyite-TiO_2 to 25 GPa.

The room-temperature post-anatase transition observed in the two studies—to an amorphous phase by Wang et al. [8,9] and to the baddeleyite polymorph in our study—is contradictory and not easily explained at the moment. If we extrapolate the trend of crystallite size versus amorphization pressure from Wang et al. work (an increase in the crystallite size had the effect of lowering the amorphization pressure in nanocrystalline anatase), our sample with a larger average crystallite size should have undergone amorphization at an even lower pressure. We do not know whether or not a ‘critical’ crystallite size is required to trigger amorphization in nanoanatase.

In Fig. 3, the variation with pressure of the relative (a/a_0 and c/c_0) unit cell constants of the nanomaterial is compared with that of macrocrystalline anatase from earlier studies [14,17]. The moderately anisotropic compressibility observed along the two crystallographic directions is clearly size-dependent: the nanocrystalline material is less compressible (on the contrary to an earlier suggestion [8]). The unit cell volume versus pressure data obtained for the nanocrystalline material are compared with that of macrocrystalline anatase [14,17] in Fig. 4. While the c/a ratio changes significantly (from 2.472 to 2.443) at pressures between 11.3 and 12.8 GPa, the volume decreases smoothly (Fig. 4). It could reflect changes in the compression mechanism of nanocrystalline anatase above 11 GPa. A fit of the volume–pressure data to a Birch–Murnaghan equation (see Ref. [17]) by assuming a pressure derivative of the bulk modulus, $K' = 4$, gave the following equation of state parameters: zero-pressure volume, $V_0 = 136.15$ Å^3 and bulk modulus, $K_T = 243(3)$ GPa. The bulk modulus obtained for the nanoanatase is about 35% larger than the corresponding value of about 180 GPa [14,17] for the macrocrystalline counterpart.

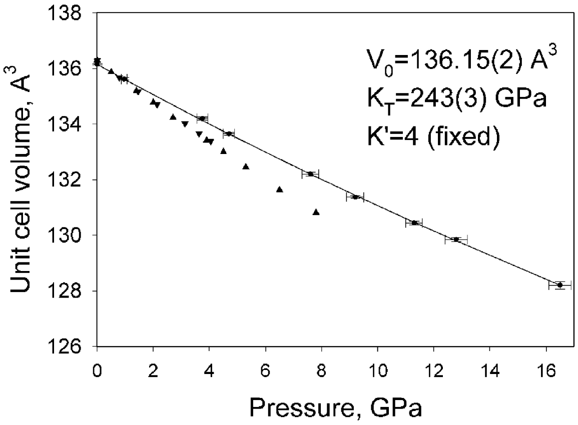

Fig. 4. Room-temperature pressure–volume data of nano-anatase (circles) compared with data from polycrystalline (triangles, from Ref. [18]) and single crystal (inverted triangle, from Ref. [15]) anatase.

Increased structural stability versus pressure with decreasing crystallite size has been demonstrated for other similar oxides. For example, in the case of macrocrystalline ZrO_2, the monoclinic to orthorhombic transition occurs at a pressure of 3.4 GPa, whereas for a ZrO_2 sample with crystallites of 29 nm, the transition pressure shifts to 6.1 GPa [18]. Over a range of pressures, both monoclinic and orthorhombic ZrO_2 phases are known to coexist dynamically [19], and this has been explained as a characteristic of a martensitic transformation [20]. We are currently investigating in detail the observed coexistence of the baddeleyite and anatase TiO_2 structures over a range of pressures, as well as the higher pressure phase transformations in nanoanatase and the accompanying crystallite size and other property changes.

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References

[1] L.-G. Liu, Science 199 (1978) 422–425.

[2] J.F. Banfield, H. Zhang, Nanoparticles and the environment, Rev. Mineral. Geochem. 44 (2001) 1–58.

[3] L.S. Dubrovinsky, N.A. Dubrovinskaia, V. Swamy, J. Muscat, N.M. Harrison, R. Ahuja, B. Holm, B. Johansson, Nature 410 (2001) 653–654.

[4] N.A. Dubrovinskaia, L.S. Dubrovinsky, R. Ahuja, V.B. Prokopenko, V. Dmitriev, H.-P. Weber, J.M. Osorio-Guillen, B. Johannson, Phys. Rev. Lett. 87 (2001) 275501-1–275501-4.

[5] J. Muscat, V. Swamy, N.M. Harrison, Phys. Rev. B 65 (2002) 224112–224126.

[6] S.C. Liao, Y.J. Chen, W.E. Mayo, B.H. Kear, Nanostruct. Mater. 11 (1999) 553–557.

[7] J. Staun Olsen, L. Gerward, J.Z. Jiang, J. Phys. Chem. Solids 60 (1999) 229–233.

[8] Z. Wang, S.K. Saxena, Solid State Commun. 118 (2001) 75–78.

[9] Z. Wang, S.K. Saxena, V. Pischedda, H.P. Liermann, C.S. Zha, J. Phys. Condens. Matter. 13 (2001) 8317–8323.

[10] A. Hammersley, Computer program FIT2D (ESRF, Grenoble), 1998.

[11] A.C. Larson, R.B. Von Dreele, Generalized crystal structure analysis system, Report LAUR 86-748, Los Alamos National Laboratory, NM, USA, 1994.

[12] L.-G. Liu, T.P. Mernagh, Eur. J. Mineral. 4 (1992) 45.

[13] K. Lagarec, S. Desgreniers, Solid State Commun. 94 (1995) 519–524.

[14] T. Arlt, M. Bermejo, M.A. Blanco, L. Gerward, J.Z. Jiang, J. Staun Olsen, J.M. Recio, Phys. Rev. B 61 (2000) 14414–14419.

[15] T. Ohsaka, S. Yamaoka, O. Shimomura, Solid State Commun. 30 (1979) 345–347.

[16] J. Haines, J.M. Leger, Physica B 192 (1993) 233–237.

[17] V. Swamy, L.S. Dubrovinsky, J. Phys. Chem. Solids 62 (2001) 673–675.

[18] S. Kawasaki, T. Yamanaka, S. Kume, T. Ashida, Solid State Commun. 76 (1990) 527–530.

[19] O. Ohtaka, T. Yamanaka, S. Kume, E. Ito, A. Navrotsky, J. Am. Ceram. Soc. 74 (1991) 505–509.

[20] M. Winterer, R. Nitsche, S.A.T. Redfern, W.W. Schmahl, H. Hahn, Nanostruct. Mater. 5 (1995) 679–688.