X-ray diffraction study on pressure-induced phase transformations in nanocrystalline anatase/rutile (TiO$_2$)

Zhongwu Wang[1,3]**, S K Saxena**[1]**, V Pischedda**[1]**, H P Liermann**[1] **and C S Zha**[2]

[1] Center for Study of Matter at Extreme Conditions (CeSMEC), Florida International University, VH-150, University Park, Miami, FL 33199, USA
[2] Cornell High Energy Synchrotron Source, Wilson Laboratory, Cornell University, Ithaca, NY 14853, USA

E-mail: zwang04@fiu.edu

Abstract
An *in situ* x-ray diffraction study was conducted to study the pressure-induced phase transformation in nanocrystalline anatase/rutile (TiO$_2$) to 35.1 GPa. The nano-anatase phase remains stable to approximately 16.4 GPa, and then transforms to an amorphous phase, which is returned upon release of pressure. The nano-rutile phase starts to transform to the baddeleyite (ZrO$_2$) structure at ∼8.7 GPa, and the transformation is complete at approximately 16.4 GPa. On release of pressure the ZrO$_2$ structure transforms to the α-PbO$_2$ structure. The results are compared to previous work on phase changes in TiO$_2$ with different particle sizes.

1. Introduction

Nanocrystalline materials are defined as materials with crystal size between 1 and 100 nm. They have attracted significant interest due to their special properties [1]. Numerous nanocrystalline metals, ceramics and semiconductors have been synthesized and studied [2, 3]. Nanocrystalline materials have larger surface to volume ratios and fewer dislocations as compared to bulk samples. There is lattice relaxation at grain boundaries. Each of these characteristics can have a significant impact on the physical and electronic properties of the material. Studies have shown that various properties such as stability, hardness, melting temperature, sintering ability, compressibility and electronic structure can be dependent upon particle size [4–9].

The mechanical, optical and electrical behaviour and vibrational modes of nano-TiO$_2$ have been widely studied [10, 12, 13]. In order to better understand the physical and vibrational
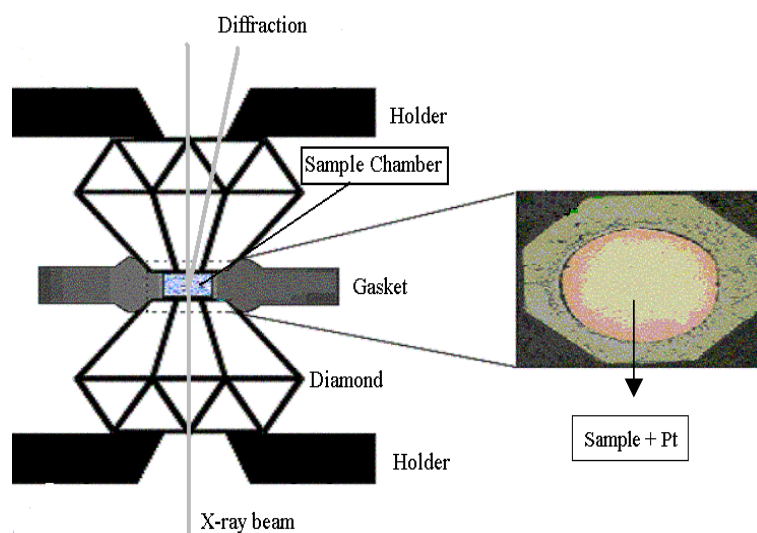
[3] Corresponding author.

Figure 1. Schematic of the high pressure experimental set-up. Pt was loaded with the sample in a DAC cell to check the pressure in each experimental run.

properties of nano-TiO$_2$, the internal strain and grain boundary structure of nano-TiO$_2$ have been extensively investigated by transmission electron microscopy, x-ray diffraction and Raman and FTIR spectroscopy [10–13]. However, there is little study on the pressure dependence of phase transformations in nano-TiO$_2$.

At ambient pressure, bulk TiO$_2$ crystallizes in three modifications: rutile, brookite and anatase. Because of the simplicity of synthesis with application in materials science (e.g. nano-techniques) and the relevance to geophysics, high-pressure behaviours of bulk anatase and rutile have been investigated experimentally by using Raman spectroscopy and x-ray diffraction [14–18]. To explore the different dynamics caused by external pressure in nanoparticle materials, we investigated the high-pressure behaviour of nano-TiO$_2$ with a mixture of anatase and rutile phase by using the diamond anvil cell (DAC) technique together with *in situ* x-ray diffraction.

2. Experiment

Commercial nanomaterials with a mixture of anatase and rutile phase with an average particle size of 30 nm were used. X-ray diffraction showed that the starting sample includes anatase and a fraction of rutile phase. However, the proportion of the two phases was not determined.

High-pressure x-ray diffraction experiments were performed at room temperature by using a gasketed high-pressure diamond anvil cell (DAC) (figure 1). Diamonds with a 400 μm culet and no bevel were used. Gasketing consisted of a hardened spring steel 400 μm thick, pre-indented to 65 μm. A hole 150 μm in diameter was packed with a mixture of nano-anatase and nano-rutile powder along with a fractional of platinum powder. Pressure was checked by the well known equation of state (EOS) of platinum (Pt). Energy dispersive x-ray diffraction spectra were collected with a fixed $2\theta (= 11°)$ on the bending magnet beam line at Cornell High Energy Synchrotron Source (CHESS), Cornell University. The energy calibration was performed with well known radiation sources, including [55]Fe and [133]Ba. The angle calibration was performed using the six peaks of standard gold (Au) powder [16].

Table 1. Phase transformations in anatase with different particle sizes.

Anatase (TiO$_2$)	High pressure phases	Transition pressure (GPa)	References
Bulk material (macro-size)	PbO$_2$ structure	2.6–4.5	[14, 17–20, 22, 25, 26]
Nanomaterial (9 nm)	Amorphous phase	~24	[15]
Nanomaterial (30 nm)	Amorphous phase	~16.4	This study

Table 2. Phase transformations in rutile with different particle sizes.

Rutile (TiO$_2$)	Transition pressure of ZrO$_2$ structure	The recovered structure at 1 atm	Reference
Bulk material (Macro-size)	13 GPa	PbO$_2$ structure	[17, 18]
Nanocrystals (30 nm)	8.7 GPa	PbO$_2$ structure	This study

3. Results and discussion

X-ray diffraction spectra of nano-crystalline anatase/rutile up to 35.1 GPa are shown in figure 2. Both anatase and rutile have tetragonal crystal structures, but belong to different space groups. Anatase has the space group $I4_1/amd$ (141) with four TiO$_2$ formula units in one unit cell, and rutile has the space group $P4_2/mnm$ (136) with two TiO$_2$ formula units in one unit cell. At one atmosphere, all peaks were assigned to the anatase and the rutile phases of TiO$_2$ [17–20]. The unit cell parameters of anatase were calculated to be $a_0 = 3.7852(3)$ Å and $c_0 = 9.5117(5)$ Å, whereas the rutile phase has unit cell parameters $a_0 = 4.5935(5)$ Å and $c_0 = 2.9581(9)$ Å. The above results are in agreement with the reports of Arlt *et al* in anatase [19] and Gerward and Olsen in rutile [17]. With increasing pressure to 8.7 GPa, peaks assigned to the baddeleyite structure (ZrO$_2$) start to arise. At a pressure of ~16.4 GPa, all rutile and anatase peaks completely disappear, and only the peaks of the ZrO$_2$ structure of TiO$_2$ remain and also become quite strong. The high-pressure x-ray diffraction pattern exhibits a very high background. The baddeleyite (ZrO$_2$) phase has a monoclinic structure, space group $P2_1/c$ (14). Based on our Raman results on the anatase with an average particle size of 9 nm [15], showing that the anatase phase becomes amorphous at a pressure of ~24 GPa, it is reasonably suggested that the high background results from the amorphization of anatase with a particle size of 30 nm in this study at a pressure of ~16.4 GPa (table 1). Thus, the baddeleyite (ZrO$_2$) structure can be explained by the pressure induced phase transformation in nano-rutile, in consideration of the same phase transformation occurring in the corresponding bulk rutile (table 2) [17].

A comparison between x-ray patterns of the high-pressure phase at 35.1 GPa and the recovered phase at ambient conditions is shown in figure 3. The results indicate that, at ambient conditions, the high-pressure ZrO$_2$ structure transforms to the α-PbO$_2$ structure, which has an orthorhombic unit cell with four TiO$_2$ molecules, space group of $Pbcn$ (60). The lattice parameters obtained were $a_0 = 4.5424(7)$ Å, $b_0 = 5.4937(5)$ Å and $c_0 = 4.9041(9)$ Å, in good agreement with the literature data reported by Arlt *et al* [19]. However, the precise phase boundary between the ZrO$_2$ and the α-PbO$_2$ structure of TiO$_2$ is not determined yet.
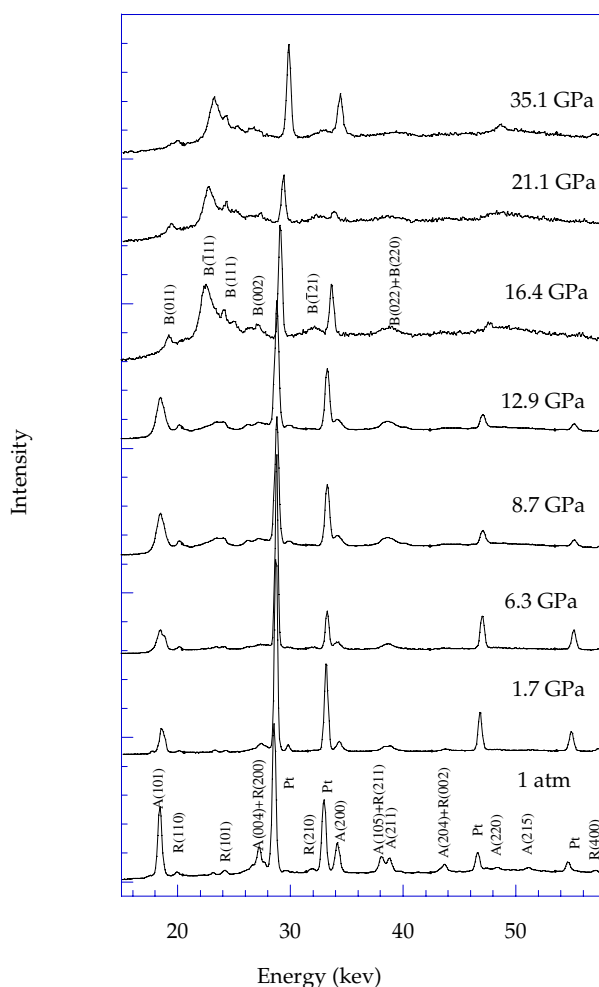
Figure 2. High pressure x-ray diffraction spectra of nano-anatase/rutile up to a pressure of 35.1 GPa at room temperature. The different phases are marked as R, rutile; A, anatase; B, baddeyelite (ZrO_2) phase; and Pt, platinum.

The amorphous phase obtained from nano-anatase at high pressures remains stable upon release of pressure to ambient conditions, as shown by the higher background.

Numerous investigations on nanometric sulphides and oxides show that there exist two types of nano-material: one type such as CdS and ZnO shows that the decrease in particle size leads to the enhancement of the transition pressure upon phase transformation [3, 5, 21], whereas the other type such as γ-Fe_2O_3 and CeO_2 exhibits the opposite effect [16, 22]. The enhancement of transition pressure with a decrease in particle size has been well explained by the contribution of a large surface energy to total internal energy, whereas the reduction of transition pressure with a decrease in particle size has been interpreted by a large volume collapse upon phase transformation [16, 22]. Our result indicates that nano-rutile is of the second type of nanometric material.

Previous studies reveal that the bulk rutile transforms to the baddeleyite (ZrO_2) phase at a pressure of 13 GPa [17, 18]. Upon decompression, this phase transforms to the α-PbO_2
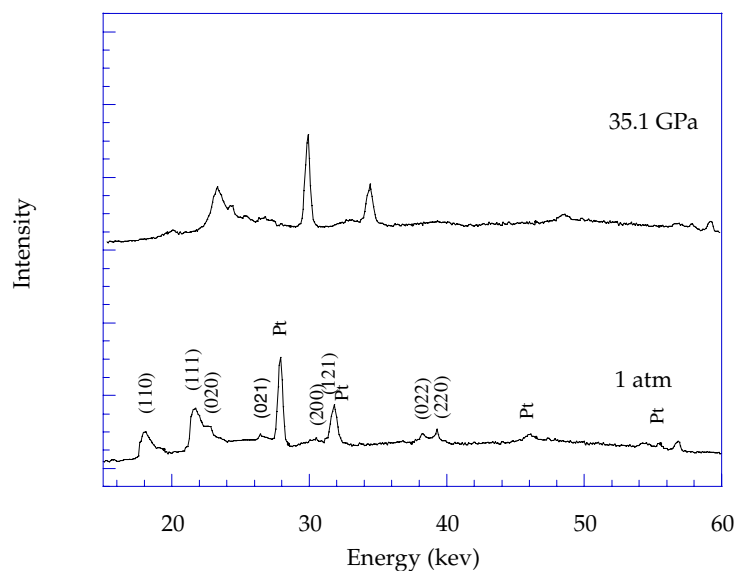
Figure 3. A comparison between the x-ray patterns of the TiO$_2$ phases obtained at 35.1 GPa and recovered at ambient conditions, respectively. The high pressure phase was fitted to the baddeleyite (ZrO$_2$) structure. The recovered phase was fitted to the α-PbO$_2$ structure with all marked peaks. Pt represents platinum.

structure at 7 GPa [17, 18]. It is clear that the transformation pressure in nano-rutile ($\sim$8.7 GPa) is lower than the pressure of 13 GPa observed in its bulk counterpart (table 2). Such observation was also discovered by Gerward and Olsen [17] with a multi-anvil high-T–P technique at *in situ* high-temperature–high-pressure conditions. In addition, the α-PbO$_2$ phase obtained at one atmosphere was also found in the bulk rutile sample [17, 18]. Combining with previous studies on nanometric CeO$_2$ and γ-Fe$_2$O$_3$ and our previous results [16, 18, 22], we found that the second type of nano-material exhibits similar high-pressure behaviour: the phases obtained at high pressures are not stable upon release of pressure. Thus, it is suggested that the reduction of transition pressure in the second type of nanometric material is most likely caused by a large volume collapse upon phase transformation and the appearance of an unstable high-pressure phase.

A large number of studies indicate that pressure-induced amorphization can happen in bulk materials in terms of high-pressure tuning [23, 24]. Such a mechanism was explained by a higher energy hindrance upon the solid–solid crystalline phase transformation as compared to the crystalline–amorphous phase transformation, which effectively prevents the formation of crystalline (structure order) phase, and then substitutes an amorphous phase (structure disorder) under high pressures [23, 24]. Other bulk materials show the opposite mechanism, exhibiting a solid–solid crystalline phase transformation, rather than an amorphous phase (figure 4). In these materials, with decrease of particle size to the nano-order, a higher surface energy as compared to the bulk counterpart significantly contributes to the total internal energy of the solid [6]. Hence, they may exhibit a similar dynamic mechanism as that happening in the bulk materials, which transform to an amorphous phase at elevated pressures. A higher energy hindrance may occur in nanomaterials upon pressure-induced solid–solid phase transformation as compared to others. This can be shown in figure 4, which exhibits the energy differences upon the corresponding phase transformations as $E_{bulk} < E_{bulk-am} < E_{nano-am} < E_{nano}$.
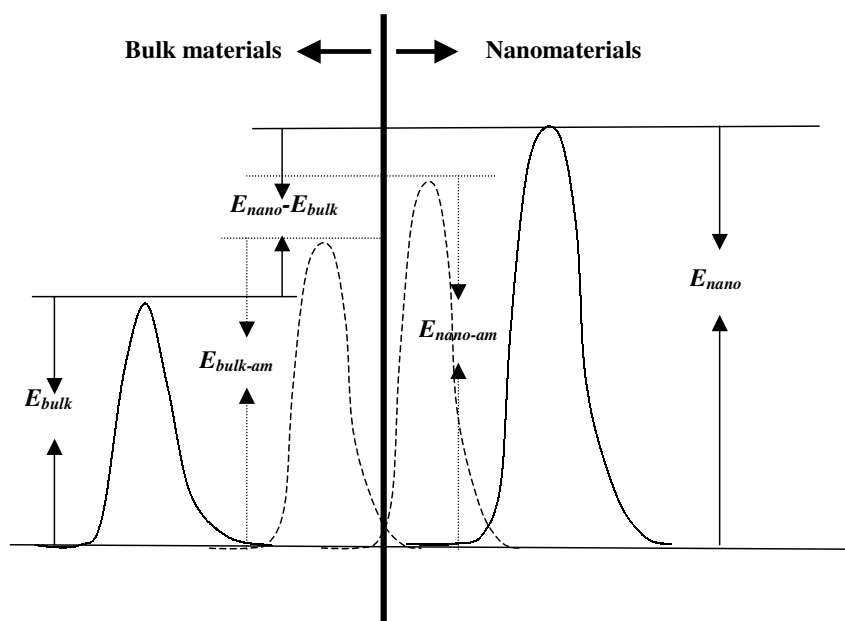
Figure 4. Schematic diagram of energy difference upon phase transformation in bulk and nanometric system. E_{bulk}, $E_{bulk-am}$, $E_{nano-am}$ and E_{nano} represent the energies upon different phase transformations (including solid crystalline to crystalline and to amorphous phases) in bulk and nanometric materials, respectively. $E_{nano} - E_{bulk}$ represents the energy difference for the same phase transformation in bulk and nanometric materials, which is higher than others, including $E_{nano-am} - E_{bulk}$, and $E_{bulk-am} - E_{bulk}$. Based on the theory of the energy minimum in this type of material, it is easily understandable that the crystal–crystal phase transformation happens in the bulk system, whereas the crystal–amorphous phase transformation happens in the nano-system.

Therefore, because of the existence of higher energy hindrance compared to other possible phase transformations, the high-pressure crystalline phase observed in the bulk system is finally substituted by an amorphous phase in the nanometric system in terms of a collapse of the original crystalline phase under strong compression. Such an explanation can be better applied in the nano-anatase phase.

Both Raman spectroscopy and x-ray diffraction studies indicate that the bulk anatase phase transforms to the orthorhombic columbite phase (α-PbO$_2$ structure) at 2.6–4.5 GPa, and then to the monoclinic baddeleyite (ZrO$_2$) structure at 13 GPa [14, 17–20, 22, 25, 26]. Upon decompression, the baddeleyite phase transforms to the α-PbO$_2$ phase at $\sim$7 GPa [19]. Compared to the bulk anatase, nano-anatase has a higher surface energy and lower defect ratios to volume [2, 3]. With our theoretical analysis, a high energy kinetic hindrance may exist in the phase transformation of the anatase-to-α-PbO$_2$ due to the size-induced effect. Thus, it is most likely to result in the structure stability of anatase over a wide range of pressure, and then transform to an amorphous phase at $\sim$16.4 GPa, rather than an α-PbO$_2$ phase or ZrO$_2$ phase at high pressures. In combination with our Raman results (table 1), showing that an amorphization occurs in nano-anatase with an average particle size of 9 nm at $\sim$24 GPa [15], it is also suggested that the reduction of particle size leads to the elevation of amorphization pressure in nano-anatase.

4. Conclusion

An *in situ* x-ray diffraction study of nanocrystalline anatase/rutile (TiO$_2$) with an average size of 30 nm has been performed up to 35.1 GPa. It is shown that the pressure-induced amorphization in nano-anatase takes place at a pressure of ~16.4 GPa. The reduction of particle size results in the structural stability of the anatase phase over a wide range of pressures. The rutile phase starts to transform to the ZrO$_2$ structure at a pressure of 8.7 GPa, and this phase transformation is complete at a pressure of ~16.4 GPa. Upon release of pressure, the ZrO$_2$ phase transforms to the α-PbO$_2$ structure. The transition pressure from the rutile to ZrO$_2$ phase is much lower than 13 GPa observed in its bulk counterpart [17, 18]. It is suggested that a higher surface energy and lower defect ratios to volume as well as the size-induced effect in nano-anatase, as compared with the bulk counterpart, may stabilize TiO$_2$ in the starting anatase phase, and then lead to the amorphization of nano-anatase under strong compression. Moreover, the phase transformation in nano-rutile may occur via a large volume collapse upon phase transformation and an unstable high pressure phase causing a reduction of transition pressure.

Acknowledgments

References

[1] Gleiter H 1989 *Prog. Mater. Sci.* **33** 223
[2] Siegel R W 1993 *Mater. Sci. Eng.* A **168** 189
[3] Alivisatos A P *et al* 1998 *Adv. Mater.* **10** 1297
[4] Chen C C, Herhold A B, Johnson C S and Alivisatos A P 1997 *Science* **276** 398
[5] Tolbert S H, Herhold A B, Brus L E and Alivisatos A P 1996 *Phys. Rev. Lett.* **76** 4384
[6] Tolbert S H and Alivisatos A P 1995 *J. Chem. Phys.* **102** 4642
[7] Qadri S B, Yang J, Ratna B R, Skelton E F and Hu J Z 1996 *Appl. Phys. Lett.* **69** 2205
[8] Jiang J Z, Gerward L, Secco R and Frost R 2000 *J. Appl. Phys.* **87** 2658
[9] Goldstein A N, Echer C M and Alivisatos A P 1992 *Science* **256** 1425
[10] Zhang W F, He Y L, Zhang M S, Yin Z and Chen Q 2000 *J. Phys. D: Appl. Phys.* **33** 912
[11] Mo S D and Ching W Y 1995 *Phys. Rev.* B **51** 13 023
[12] Bersani D, Lottici P P and Ding X Z 1998 *Appl. Phys. Lett.* **72** 73
[13] Parker J C and Siegel R W 1990 *Appl. Phys. Lett.* **57** 943
[14] Nicol M and Fong M Y 1971 *J. Chem. Phys.* **54** 3167
[15] Wang Z W and Saxena S K 2001 *Solid State Commun.* **118** 75
[16] Wang Z W, Saxena S K, Pischedda V, Liermann H P and Zha C S 2001 *Phys. Rev.* B **64** 012102
[17] Gerward L and Olsen J S 1997 *J. Appl. Crystallogr.* **30** 259
[18] Olsen J S, Gerward L and Jiang J Z 1999 *J. Phys. Chem. Solids* **60** 229
[19] Arlt T, Bermejo M, Blanco M A, Gerward L, Jiang J Z, Olsen J S and Recio J M 2000 *Phys. Rev.* B **61** 14 414
[20] Dewhurst J K and Lowther J E 1996 *Phys. Rev.* B **54** R3673
[21] Jiang J Z, Olsen J S, Gerward L and Morup S 1998 *Europhys. Lett.* **44** 620
[22] Jiang J Z, Olsen J S, Gerward L, Frost D, Rubie D and Peyronneau J 2000 *Europhys. Lett.* **50** 48
[23] Sharma S M and Sikka S K 1996 *Prog. Mater. Sci.* **40** 1 and references therein
[24] Arora A K 2000 *Solid State Commun.* **115** 665
[25] Ohsaka T, Yamaoka S and Shimomura O 1979 *Solid State Commun.* **30** 345
[26] Mammone J F, Sharma S K and Nicol M 1980 *Solid State Commun.* **34** 799