High-pressure synchrotron studies on TiO$_2$-II nanocrystallite doped with SnO$_2$

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Abstract
We have studied the high-pressure and high-temperature behaviour of α-PbO_2-type TiO_2–SnO_2 (5 mol%) nanocomposite up to 62.3 GPa and 1700 K in a laser-heated diamond-anvil cell by means of synchrotron energy-dispersive x-ray diffraction. We found that it transforms to the baddeleyite phase at 19.4 GPa at room temperature. This phase was stable up to about 40 GPa. At 62.3 GPa and 1700 K, the diffraction pattern showed that there exists another nonquenchable phase. We discussed the mechanisms for these high-pressure transformations in α-PbO_2-type TiO_2–SnO_2 (5 mol%) nanocomposite.

1. Introduction

There are four crystal forms of TiO_2 under ambient conditions: anatase, rutile, brookite, and α-PbO_2 type (TiO_2-II) [1]. At 20 GPa and 1043 K, a monoclinic baddeleyite phase was observed [2], in which the coordination number of Ti increases from 6 to 7. TiO_2 can transform to a hexagonal phase (fluorite-related) on heating at a pressure of about 25 GPa [3]. Dubrovinsky showed that a high-pressure cotunnite-structured phase of TiO_2 with the coordination number 9 could be synthesized at pressure above 60 GPa and temperatures above 1000 K; this is the hardest oxide discovered so far [4]. In previous high-pressure studies, TiO_2-II structure as a starting phase has been paid less attention because of the difficulty of its synthesis. However, high-pressure and high-temperature study of nanoscale α-PbO_2-type structure is important due to its significance in the diamond stability field [5].

Therefore the phase transition caused by compression in nanometre-scale microcrystal is also of great interest for comparison with that of bulk solid [6]. It is well known that nanocrystals are typically defect free [7] but surface or interface rich. The strain and dislocations at the interface can affect the pressure-induced structural phase transition in a finite system. The matrix surrounding the microcrystals is thought to play an important role in the pressure-induced structural phase transition and the phase stability of microcrystals [8].

In this paper, we present a structural study of the pressure-induced transformations from α-PbO$_2$-type TiO$_2$–SnO$_2$ composite at the nanometre scale to a monoclinic baddeleyite structure under lower pressure, and to an unknown structure under higher pressure and high temperature.

2. Experimental details

We prepared rutile-type TiO$_2$–SnO$_2$ nanocomposite with 5 mol% SnO$_2$ as the rutile former [9]. Rutile membranes of titania supported on SnO$_2$ may be grown epitaxially because the lattice parameters are not too different for the two systems [9–11]. Then, well crystallized TiO$_2$-II doped SnO$_2$ powder samples with average grain size 150 nm were obtained from rutile-type TiO$_2$–SnO$_2$ nanocomposite by heating at 1280 K and 5 GPa for 7 min, then quenching to room temperature under pressure. It is interesting that the α-PbO$_2$-type phase of TiO$_2$–SnO$_2$ was found to have been stabilized by the addition of Sn; it has remained stable since being synthesized 27 months ago.

The energy-dispersive x-ray diffraction (EDXD) high-pressure experiments were performed by using a symmetric diamond-anvil cell. We used stainless steel with a 200 μm hole for the gasket and ruby fluorescence shift for the pressure measurement [12]. Argon was used as the pressure medium. The high-pressure EDXD studies were performed in the NSLS at BNL.

3. Results and discussion

The EDXD data on α-PbO$_2$-type TiO$_2$–SnO$_2$ (5 mol%) and pure α-PbO$_2$-type TiO$_2$ under normal conditions are listed in table 1; they are in good agreement with literature values [13, 14].

The samples were studied for 11 steps of pressure increase up to $\sim$60.2 GPa at normal temperature. Some of the diffraction patterns are shown in figure 1. Nearly all of the high-pressure diffraction spectra up to 6.6 GPa could be indexed according to the α-PbO$_2$-type structure except an extremely anomalous line (around 2.7 Å) that overlaps with the (020) line of the α-PbO$_2$-type structure, which is attributed to solid argon (111) at approximately 5.5 GPa according to previous reports by Zou *et al* [15].

The observed intensities of the (020) peak for the α-PbO$_2$-type structure and the (111) peak for argon were greater than normal. It is well known that the (020) peak is associated with the soft stress direction of the α-PbO$_2$-type structure [16]. The (020) face in nanoscale α-PbO$_2$-type structure interspersed with argon along the (111) direction appears during the solidification of the pressure-transmitting fluid, argon. Therefore, it probably leads to preferred orientation in solid argon, which shows a poor hydrostatic pressure in DAC.

With pressure, the stronger argon reflections became broader and decrease, then apparently disappear at 43.0 GPa, which indicates a pressure-induced disordering in solid argon. The disappearance shows that argon remains more hydrostatic at higher pressures.

In addition, it is reasonable to state that the observation of the (110) rutile reflection was unexpected at the pressure of 6.6 GPa. We know that α-PbO$_2$-type TiO$_2$ can grow as an epitaxial nanometre-thick slab between twinned rutile bicrystals naturally [5]. It is possible that the stress from the preferred orientation in the pressure medium, argon, and the α-PbO$_2$-type structure leads to an additional rearrangement of the α-PbO$_2$-type lattice. This shows that there is a stress-induced lattice order in the α-PbO$_2$-type structure under high pressure.

The structural transition from the orthorhombic α-PbO$_2$-type phase to the monoclinic baddeleyite phase had its onset at 15.1 GPa and is completed at 19.4 GPa at room temperature. It can clearly be seen that the ($\bar{1}$11) line attributed to baddeleyite structure appears in the
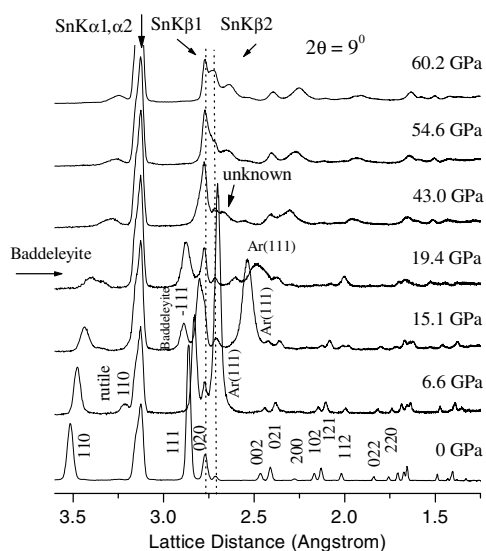
Figure 1. In the lower part of the figure the x-ray diffraction pattern of the α-PbO$_2$-type TiO$_2$–SnO$_2$ composite at 0 GPa before application of pressure is shown. The upper parts show the transformation to baddeleyite structure with increasing pressure.

diffraction pattern, which indicates that the threshold pressure of the structural phase transition is 15.1 GPa. Moreover, the diffracted intensity and line profiles were very similar for ambient and 6.6 GPa pressure, but significant decreases in diffraction intensity and broadening were observed due to the breaking up of the microcrystallites at the phase transition pressure of 15.1 GPa.

Calculation confirmed that the phase transition is accompanied by a 5.8% volume collapse. With increasing pressure, the diffraction intensity was not found to decrease; neither did the profiles of the baddeleyite structure widen or change, up to the maximum pressure obtained at room temperature. Also, the phase structure of the sample only remained stable until the highest pressure of 43.0 GPa was reached. A similar behaviour has been seen in pressure studies of rutile-type and anatase-type pure TiO$_2$ [1, 2, 17].

At 43.0 GPa, a weaker peak at $d = 2.67$ Å could not be indexed according to baddeleyite structure; it may be associated with an additional monoclinic distortion. This peak was strengthened with increase of pressure.

In order to clarify whether there is a structural transition in titania supported by heterogeneous nuclei, we carried out an experiment at a temperature exceeding $\sim$1700 K at the high pressure 62.3 GPa. The diffraction pattern and related patterns are shown in figure 2. Five lines (2.54, 2.28, 2.01, 1.82, and 1.47 Å), marked by dots in figure 2(c), appeared. They are stronger and narrower than the original lines and there are at least two additional lines, at 1.82 and 1.47 Å. The differences between the peak intensity and peak profile of the baddeleyite structure before heating and those after heating were substantial.

We know that in diamond-anvil cell (DAC) experiments, especially with solid media, samples show preferred orientations [18]. In this case, a one-sided laser-annealing technique efficiently relaxes the sample stresses and results in a quasi-hydrostatic pressure in the pressure chamber, which improves the quality of the x-ray diffraction spectra [19]; laser heating of the other side can typically cause grain growth as well as chemical reaction of materials; moreover, heating the sample is often necessary to overcome kinetic barriers to transformation [20].

We believe that the changes in diffraction patterns are due to the TiO$_2$–SnO$_2$ transformation from baddeleyite to a new structure which is different from other known structures of titania. It is reasonable to suggest that the new phase is a stable structure at high pressure and high

Table 1. The EDXD data of α-PbO$_2$-type TiO$_2$–SnO$_2$ nanocomposite and pure TiO$_2$-II. Notation: *hkl*, Miller indices; *d*, interplanar spacing (Å); *I*, integrated intensity (s, strong; m, medium; w, weak); *obs*, observed; *ref*, reference.

hkl	d_{obs} (Å)	d_{ref} (Å)[a]	d_{ref} (Å)[b]	I_{obs}	I_{ref}[a]
110	3.52	3.4980	3.50	s−	38
111	2.86	2.8482	2.85	s+	100
020	2.76	2.7510	2.75	m	7
002	2.46	2.4532	2.47	m	10
021	2.41	2.3995	2.41	m	10
200	2.28	2.2659	2.28	w−	2
102	2.17	2.1573	2.17	m	10
121	2.13	2.1206	2.12	m+	18
112	2.02	2.0085	2.01	m	10
022	1.839	1.8309	1.837	m−	6
220	1.757	1.7490	1.750	w+	5
130	1.708	1.7000	1.695	m	15
202	1.673	1.6645	1.668	m	20
221	1.655	1.6474	1.649	m	30
113	1.488	1.4815	1.49	m	14
222	1.432	1.4241	1.42	w	4
023	1.410	1.4058		m−	13
132	1.407	1.3973	1.401	m−	12
311		1.3964			12
040	1.381	1.3755		w	3
041	1.331	1.3244	1.321	w−	5
321	1.287	1.2784	1.27	w−	2
312	1.259	1.2525		w−	3
	$a = 4.55(5)$	$a = 4.532$	$a = 4.55$		
	$b = 5.52(7)$	$b = 5.502$	$b = 5.46$		
	$c = 4.93(3)$	$c = 4.906$	$c = 4.92$		
	$V = 124.2$	$V = 122.3$	$V = 122.2$		

[a] Using Ti$_3$O$_5$ dissolved in sulphuric acid at elevated temperatures [13].
[b] Synthesis using shock-wave pressures [14].

temperature. The crystallographic unit-cell parameters for the two structures may be the same over the narrow pressure and temperature range in which the two phases were observed to coexist.

No indication of chemical reaction between the Ti and Sn was observed. The diffraction patterns of the sample after decompression confirm a lack of chemical reaction.

The diffraction patterns of samples were studied down to ambient conditions with the pressure decreased in three steps, as shown in figure 3. The new peaks of the unknown new phase and their features disappeared on decompression at 40.9 GPa. The results indicated that the crystallographic unit-cell parameters for the new phase and the baddeleyite structures were similar over the higher-temperature range in which the two phases were observed to coexist. The new phase appears to show stability under high temperature and high pressure, which disappears with temperature quenching.

On release of pressure, the mixture phases of α-PbO$_2$-type and baddeleyite structure were observed down to about 16.7 GPa, which is similar to our observations regarding the pressure of 19.4 GPa when increasing pressure—with no evidence of the high-pressure phase being present. With decompression at ambient pressure, the structure of the sample was restored completely to the α-PbO$_2$-type structure.
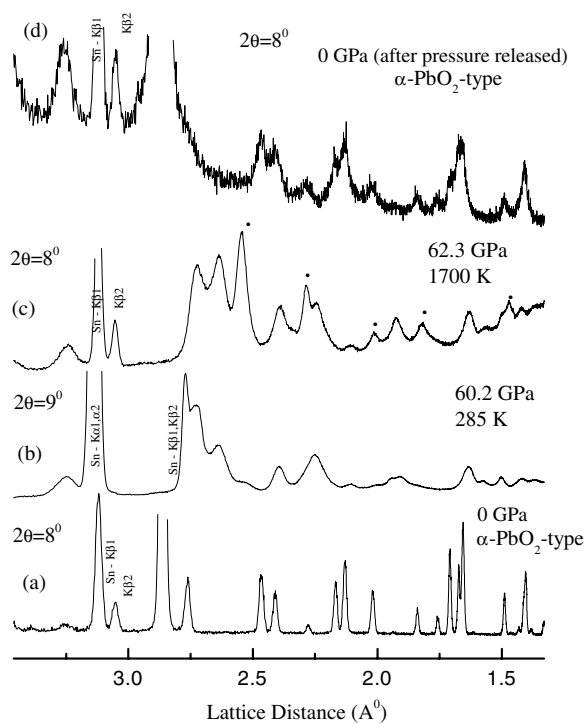
Figure 2. EDXD of the starting materials: α-PbO$_2$-type TiO$_2$–SnO$_2$ (a); TiO$_2$–SnO$_2$ structure at 60.2 GPa and ambient temperature (b); TiO$_2$–SnO$_2$ with a new structure at 62.3 GPa and 1700 K (c); and decompression of TiO$_2$–SnO$_2$ under ambient conditions to give α-PbO$_2$-type structure (d).
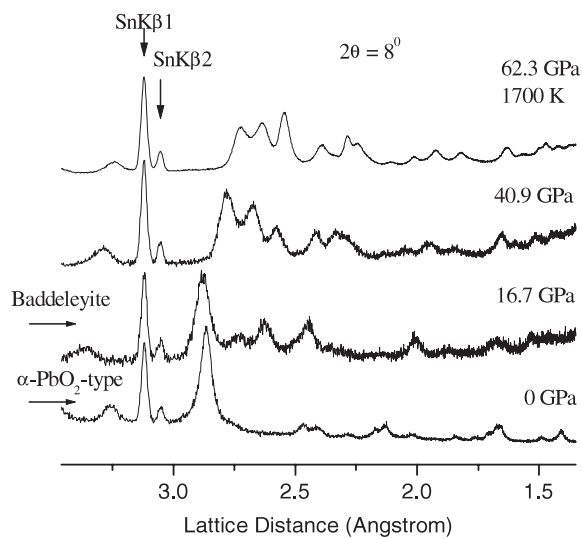

Figure 3. The upper parts show the structure at high pressure after heating; the lower parts show the baddeleyite structure decompressions and α-PbO$_2$-type phase at 0 GPa after pressure was released.
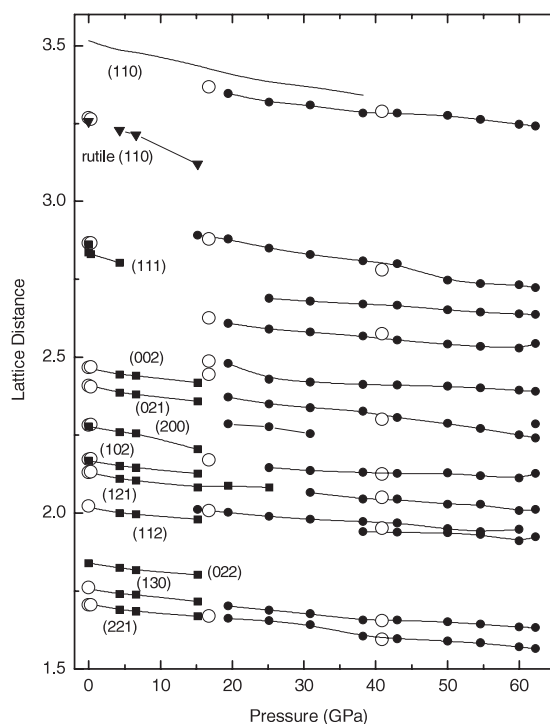
Figure 4. Lattice distance versus pressure. Solid and open circles indicate measurements taken on compression and decompression, respectively, whereas the solid squares indicate the α-PbO$_2$-type phase; solid circles indicate the baddeleyite phase of TiO$_2$ and the new phase.

Figure 4 shows the evolution of the lattice distance for the sample under pressure. Solid and open symbols indicate measurements taken on compression and decompression. The decompression values were generally close to the line obtained for compression. The phase transformation to baddeleyite structure at about 20 GPa and room temperature was observed without pressure hysteresis.

4. Summary

Stress-induced lattice ordering of α-PbO$_2$-type TiO$_2$–SnO$_2$ composite to form rutile-type structure was found at 6.6 GPa.

A phase transition from the α-PbO$_2$-type phase to the baddeleyite phase at 15.1 GPa was observed.

At 62.3 GPa pressure, TiO$_2$–SnO$_2$ composite may undergo a structural transformation not seen for pure TiO$_2$, that is kinetically sluggish but is aided by laser heating at 1700 K. The resulting structure is only stable at high temperature and high pressure.

The features of the structural transition of TiO$_2$–SnO$_2$ nanocomposite at temperature above 1700 K and the pressure of 62.3 GPa are significantly different from those reported for pure TiO$_2$. The slight SnO$_2$ impurities may be the reason for this difference.

Above 43.0 GPa pressure, there might be a distortion of the baddeleyite structure, which needs to be investigated further. Additional experimental studies are planned to address the structure of this phase, which will have important ramifications as regards understanding and expanding the titania pressure-based phase diagram.

Acknowledgment

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