PHYSICAL REVIEW B VOLUME 49, NUMBER 14 1 APRIL 1994-II

New high-pressure and -temperature phase of ZrO_2 above 1000 °C at 20 GPa

O. Ohtaka and T. Yamanaka
College of General Education, Osaka University, 1-1 Machikaneyama, Toyonaka, Osaka 560, Japan

T. Yagi
Institute for Solid State Physics, University of Tokyo, 7-22-1 Roppongi, Minato-ku, Tokyo 106, Japan

(Received 27 July 1993)

Combining a diamond anvil cell and a laser heating system, pure ZrO_2 powders were heated above 1000 °C under high pressures above 20 GPa. Thermally quenched samples were investigated by using x-ray diffraction under high pressure. The results indicated that a new high-pressure phase was formed. This new phase was retained in the course of releasing pressure down to 1 GPa but reverted to the monoclinic phase on the complete release of pressure. Thirteen diffraction lines were confirmed to be from the new phase and indexed on the basis of hexagonal symmetry. The molar volume of this phase is larger than that of orthoII, which appears in the low-temperature region of the same pressure range. Its structure is derived from that of orthoII which is composed of pseudohexagonal packing of oxygen.

I. INTRODUCTION

ZrO_2 is one of the major components of modern ceramic materials. Its high-temperature forms, tetragonal and cubic ZrO_2, have been extensively studied and used by industry. Recently, phase transition of ZrO_2 under high pressure has gathered much interest in both material and geophysical researches. Because the toughening mechanism of ZrO_2 ceramics is explained by a stress-induced phase transition,[1,2] the phase transition at high pressure is to be studied from a microscopic viewpoint. The investigation of high-pressure polymorphism of ZrO_2 is also important in geophysical implications as the polymorphic structure of ZrO_2 might be a possible candidate for the high-pressure form of SiO_2.[3,4]

ZrO_2 has a monoclinic symmetry at ambient conditions and, as schematically shown in Fig. 1, three high-pressure polymorphs of orthoI,[5] orthoII,[3] and tetragonal[6] have been reported. The monoclinic-to-orthoI phase transition is given rise to by compression above 3 GPa at room temperature.[5,7–13] Based on a neutron powder diffraction experiment of orthoI quenched to ambient conditions, the space group of this phase was determined to be *Pbca* and structure refinement was performed.[14] OrthoI has a distorted fluorite structure similar to that of monoclinic ZrO_2 and the phase transition between them shows the characteristics of a martensitic transition. OrthoII is stable above 13 GPa at 800 °C and isostructural with cotunnite ($PbCl_2$).[3,13,15–18] The orthoI-to-orthoII phase transition is accompanied by a nucleation and growth process.[13] Consequently, heating or excessive compression is required to promote this transition. On the other hand, once orthoII is formed under high pressure, it can be easily quenched to ambient conditions. The tetragonal phase, which is different from that of the ordinary high-temperature form at ambient pressure, appears at pressures greater than 35 GPa.[6] This phase is stable to at least 60 GPa and quenchable to ambient conditions. Its accurate structure, however, has not yet been determined.

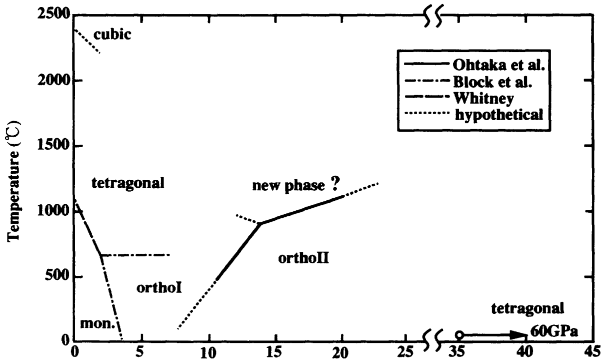


FIG. 1. Pressure-temperature phase diagram of ZrO_2. Monoclinic-to-tetragonal (high-temperature form) is after Witney (Ref. 23); monoclinic-to-orthoI and orthoI-to-tetragonal are after Block *et al.* (Ref. 8); orthoI-to-orthoII and orthoII-to-high-temperature phase (denoted as "new phase?") are after Ohtaka *et al.* (Ref. 13); tetragonal phase which appears above 35 GPa is after Arashi *et al.* (Ref. 6).

These studies of ZrO_2 under high pressure have mainly been made at room temperature or, at most, a few hundred °C. An experimental study of the phase relations at a higher-temperature region was first reported by Ohtaka *et al.*[13,18] Throughout the synthesis experiments of orthoII, they showed that the monoclinic phase was recovered by heating above about 1000 °C in the pressure range where orthoII is expected to be stable. They also reported that, in the course of raising temperature, abrupt discontinuities in electrical conductivity were observed around 1000 °C at 16.5 GPa and around 1050 °C at 18 GPa. These results suggest that orthoII transforms to another, unquenchable, high-pressure and temperature phase at temperatures as high as about 1000 °C (denoted as "new phase?" in Fig. 1). Furthermore, the results of synthesis experiments imply that this phase does not re-

0163-1829/94/49(14)/9295(4)/$06.00

vert to orthoII by thermal quench under high pressure. In the present study, the authors attempted the *in situ* x-ray-diffraction observations of ZrO_2 which was preheated above 1000 °C with a YAG laser under high pressure.

II. EXPERIMENT

The starting material was a fine powder of >99.9% pure ZrO_2 (grain size is about 100 nm) provided by Tosoh Co. The powder had a purity of more than 99.9%. It was mixed with about 1 wt % of platinum black, which works as an absorber of the YAG laser for heating.

A lever and spring-type diamond anvil apparatus[19] was used throughout the high-pressure experiments. The anvils were one-third carat and Drukker standard-cut diamonds with a 0.5-mm culet. Stainless steel of 0.2 mm in thickness was used as a gasket. The sample was placed in the gasket hole of 0.25 mm in diameter without any pressure transmitting medium to keep a hydrostatic condition because of too high pressures over 20 GPa in all present runs. The generated pressure was measured by the ruby fluorescence method.[20]

After compression above 20 GPa, the sample was heated by using a YAG laser. The sample temperature was estimated to be above 1000 °C from the radiation emitted from the sample. A thin laser beam of 15 μm in diameter from the 12 W single-mode YAG laser was scanned to heat the whole area of the sample and the total heating duration was about 1 h.

High-pressure *in situ* x-ray-diffraction measurements were undertaken at room temperature with a high-power rotating-anode x-ray generator operated at 55 kV and 160 mA. Filtered Mo$K\alpha$ radiation was collimated with a 0.1-mm pinhole. An x-ray-diffraction pattern was recorded on a Debye-Scherrer camera with a radius of 57.3 mm. The typical exposure time was 12 h.

Two individual runs were performed in order to confirm reproducibility. Initial values of the compression were 26 and 27 GPa for the first and the second runs, respectively. After the laser heating, however, pressures in the sample chamber were decreased to 20 and 21 GPa for respective runs. In the course of decompression, x-ray-diffraction patterns were recorded approximately by every 5 GPa. After the complete release of pressure, recovered samples were investigated by using a microfocused x-ray diffractometer.

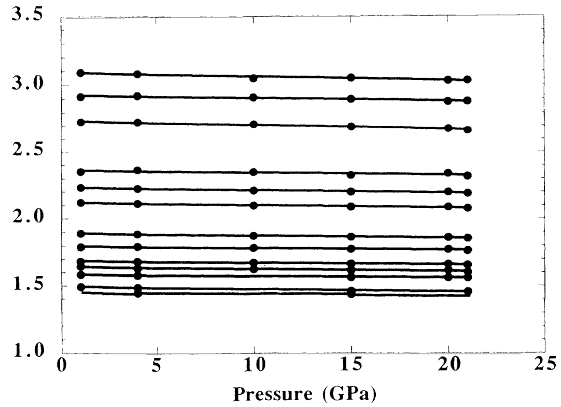


FIG. 2. Pressure dependence of observed *d* spacings.

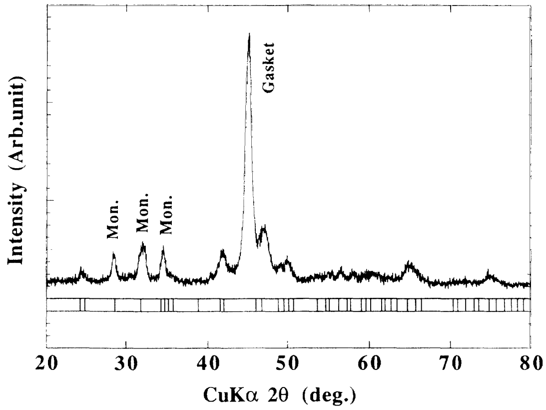


FIG. 3. X-ray-diffraction pattern of recovered sample.

II. RESULTS AND DISCUSSION

Figure 2 shows the pressure dependence of the observed *d* spacings. The same diffraction patterns were observed in both runs. These patterns were retained and no additional diffraction lines appeared in the course of releasing pressure down to 1 GPa. Though a few diffraction lines were not detected on the x-ray films of short exposure time, 13 lines were confirmed to be diffracted from the sample. The observed x-ray-diffraction pattern differs completely from those of any polymorphs reported so far for ZrO_2.[6,10,13,14] These results indicate the new high-pressure and -temperature phase of ZrO_2 was quenched to room temperature under compression.

Since this high-pressure diffraction study was made without any pressure transmitting medium, the new phase may be induced by shear stress similar to the other stress-induced transition of ZrO_2.[1,2] The reproducibility of the phase transformation indicates the new phase may have a thermodynamically stable region.

TABLE I. Observed and calculated *d* spacings for ZrO_2 in hexagonal high-pressure and -temperature phase ($Z=8$). $a_0=6.77(2)$, $c_0=6.84(3)$, and $V=271.4(2)$ Å^3.

H,K,L		*d* obs.	*d* calc.
111	*W*	3.09	3.03
200	*VS*	2.93	2.93
201	*S*	2.74	2.69
112	*VW*	2.37	2.41
202	*W*	2.23	2.23
103	*S*	2.12	2.13
113	*M*	1.89	1.89
203	*W*	1.80	1.80
220	*M*	1.69	1.69
221	*W*	1.64	1.64
213	*M*	1.58	1.59
303	*W*	1.49	1.48
204	*W*	1.48	1.48

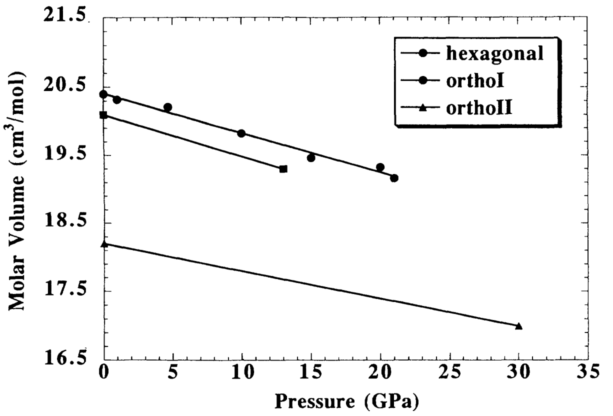
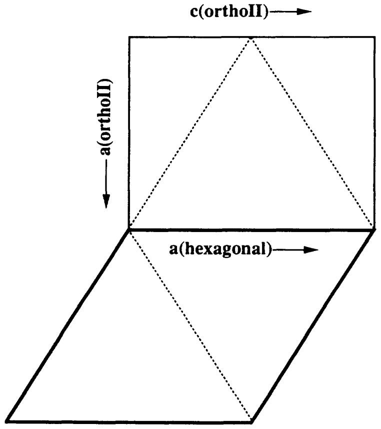


FIG. 4. Pressure dependence of molar volume of high-pressure phases of ZrO$_2$. Those for orthoI and orthoII are after Ming and Manghnani (Ref. 22).

The x-ray-diffraction pattern of the recovered sample is shown in Fig. 3. The sample was held in the gasket and a diffraction from the gasket was observed together with those from the sample. The rows of markers below the pattern show the peak positions of the monoclinic phase.[21] Though it is difficult to identify weak peaks especially in the high-angle region, all strong diffraction lines except that from the gasket were indexed as the monoclinic phase and no diffractions corresponding to the high-pressure phase were observed. Peaks indexed as "Mon." in Fig. 3 are the reported three strongest diffractions of the monoclinic structure.[21] The broad diffraction lines indicate that the crystallite size of the sample is less than 100 nm.

It is concluded that a new high-pressure phase was formed by laser heating under high pressure and retained in the course of releasing pressure and then reverted to the monoclinic phase directly on the complete pressure release. The present result that the monoclinic phase was recovered is consistent with the results of previous quench experiments.[13]



$c_{\text{hex.}}$ (6.84Å) $\approx 2\,b_{\text{orthoII}}$ (2×3.33=6.66Å)

$a_{\text{hex.}}$ (6.77Å) $\approx c_{\text{orthoII}}$ (6.47Å)

$\approx \frac{2}{\sqrt{3}} a_{\text{orthoII}}$ ($\frac{2}{\sqrt{3}}$×5.58 = 6.44Å)

FIG. 5. Hexagonal unit cell derived from orthoII unit cell. Lattice constants of orthoII are after Suyama *et al.* (Ref. 9).

By extrapolating the pressure dependence of observed *d* spacings shown in Fig. 2, *d* spacings of this new phase at ambient conditions were obtained and indexed on the basis of hexagonal symmetry as shown in Table I. Comparing the unit-cell volumes among ZrO$_2$ polymorphs,[3,6,14] 8 ZrO$_2$ molecules are considered to be involved in the unit cell.

Using the determined unit cell, the pressure dependence of the molar volume is obtained as shown in Fig. 4. In this figure, the values reported for orthoI and orthoII are also shown.[22] The density of the newly observed hexagonal high-pressure phase is about 10% lower than that of orthoII and about 1% lower than orthoI.

From the pressure dependence of V/V_0, the compressibility of the hexagonal high-pressure phase is indicated to be similar with that of orthoI and larger than that of orthoII.

The plausible crystal structure for the new phase was investigated based on the obtained unit cell with hexagonal symmetry. As this new phase is transformed from orthoII by heating and, furthermore, orthoII has pseudohexagonal packing of O atoms,[3] we attempted to relate these two structures. We tried the indexing of the diffraction peaks by possible several structure models. It is most likely that hexagonal phase is formed from orthoII by becoming higher symmetry at elevated temperature. The structures of hexagonal phase and orthoII are related by setting the *b* and *c* axes of orthoII parallel to the *c* and *a* axes of the hexagonal phase, respectively. The hexagonal unit cell derived from the orthoII unit cell is schematically shown in Fig. 5. The lattice constants of the hexagonal phase are compared with those of orthoII (Ref. 9) and indicated in this figure. In this hexagonal structure, a Zr atom is considered to be coordinated by 9 O atoms as well as in orthoII.

IV. CONCLUSIONS

By laser heating above 1000 °C under high pressure, a new high-pressure and -temperature phase of ZrO$_2$ was formed. *In situ* x-ray-diffraction observation revealed that this new phase is metastably retained in the course of releasing pressure down to 1 GPa but reverts to the monoclinic phase directly on the complete release of pressure. The observed x-ray-diffraction pattern of this phase is indexed on the basis of hexagonal symmetry. The molar volume and the compressibility of this phase are both larger than those of orthoII, which appears at the low-temperature region of the same pressure range. The hexagonal structure of this phase is considered to be derived from that of orthoII which has pseudohexagonal packing of O atoms. However, the accurate structure of this new phase has not yet been determined.

ACKNOWLEDGMENTS

We are grateful to Dr. W. Utsumi and Dr. H. Yusa for their help in the course of high-pressure experiments.

[1] T. K. Gupta, F. F. Lange, and J. H. Bechtold, J. Mater. Sci. **13**, 1464 (1978).

[2] W. M. Kriven, J. Am. Ceram. Soc. **71**, 1021 (1988).

[3] L. Liu, J. Phys. Chem. Solids **41**, 331 (1980).

[4] L. Liu and W. A. Basset, *Elements, Oxides, and Silicates: High-Pressure Phases with Implications for Earth's Interior* (Oxford University Press, New York, 1986), p. 250.

[5] G. Bocquillon and C. Susse, Rev. Int. Hautes Temp. Refract. **6**, 263 (1969).

[6] H. Arashi, T. Yagi, S. Akimoto, and Y. Kudoh, Phys. Rev. B **41**, 4309 (1990).

[7] H. Arashi and M. Ishigame, Phys. Status Solidi A **71**, 313 (1982).

[8] S. Block, J. A. H. da Jornada, and G. J. Piermarini, J. Am. Ceram. Soc. **68**, 497 (1985).

[9] R. Suyama, T. Ashida, and S. Kume, J. Am. Ceram. Soc. **68**, C314 (1985).

[10] Y. Kudoh, H. Takeda, and H. Arashi, Phys. Chem. Miner. **13**, 233 (1986).

[11] B. Alzyab, C. H. Perry, and R. P. Inel, J. Am. Ceram. Soc. **70**, 760 (1987).

[12] O. Ohtaka, S. Kume, T. Iwami, and K. Urabe, J. Am. Ceram. Soc. **71**, C164 (1988).

[13] O. Ohtaka, T. Yamanaka, S. Kume, E. Ito, and A. Navrotsky, J. Am. Ceram. Soc. **74**, 505 (1991).

[14] O. Ohtaka, T. Yamanaka, S. Kume, N. Hara, H. Asano, and F. Izumi, Proc. Jpn. Acad. B **66**, 193 (1990).

[15] O. Ohtaka, S. Kume, and E. Ito, J. Am. Ceram. Soc. **71**, C448 (1988).

[16] S. R. U. Devi, L. C. Ming, and M. H. Manghnani, J. Am. Ceram. Soc. **70**, C218 (1987).

[17] H. Arashi, T. Suzuki, and S. Akimoto, J. Mater. Sci. Lett. **6**, 106 (1987).

[18] O. Ohtaka, S. Kume, and E. Ito, J. Am. Ceram. Soc. **73**, 744 (1990).

[19] T. Yagi, T. Suzuki, and S. Akimoto, J. Geophys. Res. **90**, 8784 (1985).

[20] H. K. Mao, P. M. Bell, J. W. Shaner, and D. J. Steinberg, J. Appl. Phys. **49**, 3276 (1978).

[21] D. K. Smith and H. W. Newkirk, Acta Crystallogr. **18**, 983 (1965).

[22] L. C. Ming and M. H. Manghnani, *Solid State Physics Under Pressure: Recent Advance in Anvil Devices* (KTK Scientific, Tokyo, 1985), p. 135.

[23] E. D. Witney, J. Electrochem. Soc. **112**, 91 (1965).