PHYSICAL REVIEW B VOLUME 48, NUMBER 1 1 JULY 1993-I

# Pressure-induced phase transitions and volume changes in $HfO_2$ up to 50 GPa

J. M. Leger, A. Atouf, P. E. Tomaszewski,* and A. S. Pereira†
*Laboratoire de Physico-Chimie des Matériaux, 1, pl. A. Briand, 92190 Meudon, France*

(Received 18 November 1992)

The phase transformations and pressure-volume dependence of $HfO_2$ have been investigated at room temperature by angle-dispersive powder x-ray diffraction under high pressure to 50 GPa in a diamond anvil cell. The phase transformation from the monoclinic I (baddeleyite) to orthorhombic phase II was observed around 10 GPa. This phase is stable up to 26 GPa where it transforms to a new phase III with another orthorhombic unit cell. At about 42 GPa, a third phase transition occurs to phase IV of tetragonal symmetry. The pressure dependences of the cell parameters and volume have been determined. The successive volume discontinuities are 2.5%, 2.5%, and 5%, respectively. The bulk moduli of all the phases have been calculated from Birch's equation of state and are discussed. The high-pressure phases were found to be metastable at normal pressure. No orthorhombic cotunnite-type structure was observed under pressure at room temperature. Although the structural properties of $HfO_2$ and $ZrO_2$ are similar at lower pressures, their evolutions are different above 20 GPa.

## INTRODUCTION

Hafnia ($HfO_2$) is considered to be very similar to zirconia ($ZrO_2$) in chemical, physical, and structural properties. Thus there have been few studies made on hafnia itself, especially at high pressures. Most of the high-pressure experiments have been devoted to zirconia as this compound is extremely important in the production of tough ceramics,[1] and the understanding of its phase behavior is of prime importance. In this way, high-pressure studies have been used not only for the determination of the phase boundaries but also to get information about the transition mechanisms.[2-5] The pressure-temperature (*P-T*) phase diagram of $ZrO_2$ has been extensively studied in broad ranges of temperatures and pressures (see Ref. 6 and references therein). The similar *P-T* diagram for hafnia, which also has high potential as a refractory compound, was studied only up to 6 GPa.[7-9] Recently, however, a few experiments were made at room temperature up to higher pressures, of 12 (Ref. 10) and 20 GPa,[11] but the volume-dependence results are of limited accuracy (see below). A better understanding of the high-pressure behavior of $HfO_2$ is important not only to clarify its own phase diagram, but also to learn about the evolution under very high pressure of similar structures at normal pressure. In addition, the identification of dense structures is very important from the geophysical point of view: the dense packed structures of dioxides (e.g., $SiO_2$) are still now known.

At normal pressure, hafnia and zirconia are monoclinic at room temperature and transform to a tetragonal structure at intermediate temperatures (about 1900 and 1300 K for hafnia and zirconia, respectively) and then to a cubic structure at higher temperatures (about 2800 and 2700 K, respectively). The crystal structure of $HfO_2$ was determined and refined several times at room temperature.[11-13] It is basically the same as that of monoclinic zirconia. The cell parameters are $a=5.1170$ Å, $b=5.1754$ Å, $c=5.2915$ Å, $\beta=99.21°$ and the space group is $P2_1/c$ (No. 14).[13]

At high pressure, a phase transition was discovered in $HfO_2$ at around 800 K and 6 GPa.[7] Recent Raman results[14] showed the appearance of a high-pressure phase at about 4.3 GPa at room temperature and persistence up to the upper limit of those experiments, i.e., 9.5 GPa. The structure of this phase was determined by Rietveld analysis of x-ray diffraction data from a quenched sample at normal pressure.[9,15] The best solution was obtained with the space group *Pbca* (No. 61) and lattice parameters: $a=10.0172$, $b=5.2276$, and $c=5.0598$ Å.[9] Until now this result was not confirmed by *in situ* studies. Notice that the experiments with lower resolution can easily yield the *a* parameter two times smaller than the correct value. There is also a report of another high-pressure high-temperature phase which was found to be quenchable to ambient conditions, for which the lattice parameters are $a=3.311$, $b=5.550$, and $c=6.461$ Å and the orthorhombic space group was supposed to be of the *Pmnb* (No. 62) group as in the cotunnite-type structure.[2] However, it is evident that the results obtained from quenching experiments, far from thermodynamic equilibrium, should be taken with caution. In addition, the presence of shear stresses, the influence of the pressure transmitting medium (especially water), and some inaccuracy in the estimation of the pressure and temperature values can be present. The scarce *in situ* results[10,14] for hafnia under pressure are not conclusive about the possible phase transitions, either by limitations in the highest attainable pressure or low resolution in the analytical techniques.

Would the similarities between zirconia and hafnia at normal pressure manifest into similar behavior at much higher pressures? In any case, a rich phase diagram could be expected for hafnia as in the case of zirconia. Thus we have performed *in situ* high-pressure x-ray diffraction studies up to 50 GPa.

0163-1829/93/48(1)/93(6)/$06.00

## EXPERIMENTAL PROCEDURE

The *in situ* powder x-ray diffraction experiments were performed at room temperature using a diamond anvil cell of the lever-arm type with diamonds of 500-$\mu$m flats. The hafnium oxide sample was a spectroscopic grade powder from Johnson Matthey Co. with a grain size of a few micrometers as estimated visually.

The sample was mixed with silicon oil in order to reduce anisotropic stress components at high pressures. Indeed, the 4:1 methanol-ethanol mixture generally used as pressure transmitting medium introduces some discontinuities in the resulting data, when it solidifies at room temperature at around 10–12 GPa.[16] The silicon-oil-sample mixture was loaded in the 150-$\mu$m-diam hole drilled in a T301 gasket of initial thickness 250 $\mu$m, preintended to 100 $\mu$m. A single-crystal ruby chip was placed on the upper surface of the sample as the pressure calibrant. The value of the pressure was calculated from the fifth power of the wavelength shift of the $R_1$ fluorescence line[17] (fit with anisotropic stress component) although the two maxima of the doublet were always clearly seen.

The zirconium-filtered molybdenum radiation from a fine focus x-ray tube was used. The diameters of the Debye rings in the diffraction patterns were measured with a micrometer under a low magnification microscope.[16] In order to make a more precise evaluation of relative intensities of the strongest lines, optical microdensitometry was performed on some films. Most of the experimental data were obtained upon increasing the pressure; a few additional patterns were recorded upon releasing the pressure. The uncertainties are estimated to be ±0.7% in volume and ±0.1 GPa in pressure.

The powder diagram was indexed using the DICVOL program.[18] The diffraction lines which possibly coincided with the lines from the gasket (mostly iron) were omitted in the discussion of our data and are not plotted in the corresponding figure.

The experimental data on the pressure dependence of the relative volume $V/V_0$ obtained with increasing pressure were fitted in each phase to Birch's equation of state[19] (few data were analyzed upon decreasing the pressure because several phases coexisted down to normal pressure):

$$P=\tfrac{3}{2}B_0x(1+x)^{5/2}(1+\alpha x) ,$$

where $x=(V/V_0)^{-2/3}-1$, $\alpha=\frac{3}{4}(B_0'-4)$. $B$ is the bulk modulus and $B'$ its first pressure derivative; the subscript zero refers to values at normal pressure.

## RESULTS AND DISCUSSION

### Pressure dependence of unit cell parameters and volume

All basic experimental data, i.e. $d$ spacings calculated from the position of diffraction lines on the x-ray films, are plotted versus pressure in Fig. 1. Four pressure regions are clearly seen; they correspond to different phases with transition pressures of about 10, 27, and 40 GPa.

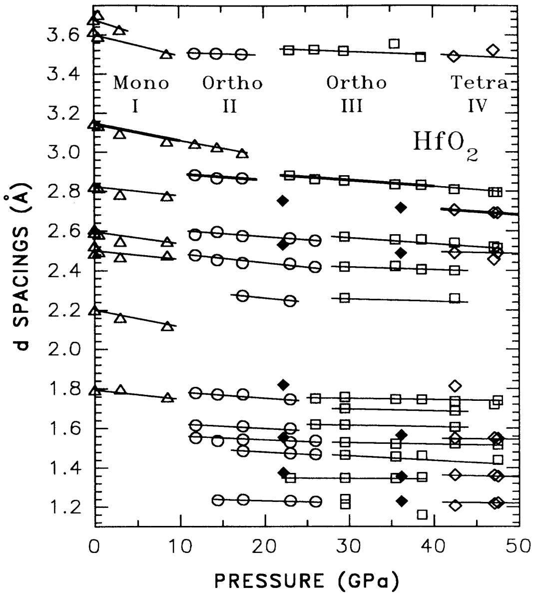

FIG. 1. Variations in the interplanar distances $d$ of $HfO_2$ with pressure. Open symbols: increasing pressure; filled symbols: decreasing pressure; △: monoclinic phase I; ○: orthorhombic phase II; □: orthorhombic phase III; ◇: tetragonal phase IV. The lines are a guide to the eye. The thick line represents the highest-intensity line in each phase.

The upper two transitions and high-pressure phases were not known until now.

We have been able to record 10, 11, 14, and 7 characteristic lines for the high-pressure phases I, II, III, and IV, respectively, which was sufficient in order to allow the lines to be indexed. The number of lines effectively observed at each pressure could be less depending on the quality of the diffraction pattern. The interplanar distances and their indices $hkl$, the corresponding lattice parameters for each phase, are presented in Table I. The pressure dependences of the lattice parameters and unit cell volume are displayed in Figs. 2 and 3, respectively. A few additional lines of the high-pressure range could be indexed as lines from the lower-pressure phase, which indicates broad ranges of coexistence between phases.

The first transition, from phase I (monoclinic) to phase II (orthorhombic), appears at much higher pressure (10 GPa) than the 4.3 GPa observed in experiments with a single crystal.[14] However, it is in agreement with Raman experiments performed on a pellet of precompacted powder where the transition was not detected up to 12 GPa.[10] Thus the transition pressure is strongly dependent on the crystalline size, the environment of the sample, and probably its history. A similar dependence has already been reported for the equivalent transition in $ZrO_2$.[3,4]

The volume data for the different phases were fitted to the Birch equation of state,[19] while assuming the usual value of 5 for the first pressure derivative of the bulk modulus and using the volumes observed from the recovered sample as the reference values for normal pres-

TABLE I. Interplanar distances (Å) with their indices and unit cell parameters for each phase of $HfO_2$ under high pressure (*: line of highest intensity; *m*: line from the monoclinic phase; ort: line from the orthorhombic phase III).

| Phase | | I | | | II | | | III | | | IV | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *P* (GPa) | | mono | | | ortho | | | ortho | | | tetra | |
| | | 8.5 | | | 17.4 | | | 29.5 | | | 42.5 | |
| | | $d_{obs}$ | $d_{cal}$ | | $d_{obs}$ | $d_{cal}$ | | $d_{obs}$ | $d_{cal}$ | | $d_{obs}$ | $d_{cal}$ |
| | 110 | 3.503 | 3.520 | 210 | 3.503 | 3.541 | 020 | 3.519 | 3.515 | 110 | 3.529 | 3.521 |
| | $11\bar{1}$ | 3.056* | 3.062 | *m* | 2.996 | | 120 | 2.853* | 2.846 | ort | 2.809 | |
| | 111 | 2.827 | 2.813 | 211 | 2.866* | 2.882 | 111 | 2.570 | 2.579 | 111 | 2.705* | 2.714 |
| | 020 | 2.547 | 2.535 | 020 | 2.573 | 2.565 | 200 | 2.419 | 2.425 | ort | 2.54 | |
| | 102 | 2.477 | 2.459 | 400 | 2.438 | 2.447 | 210 | 2.262 | 2.292 | 200 | 2.489 | 2.490 |
| | $12\bar{1}$ | 2.120 | 2.116 | 021 | 2.274 | 2.278 | 040 | 1.758 | 1.758 | ort | 2.40 | |
| | $12\bar{2}$ | 1.758 | 1.765 | 420 | 1.771 | 1.771 | 002 | 1.700 | 1.690 | 112 | 1.810 | 1.822 |
| | 212 | 1.602 | 1.604 | 230 | 1.611 | 1.614 | 300 | 1.618 | 1.617 | ort | 1.737 | |
| | | | | 231 | 1.543 | 1.535 | 022 | 1.530 | 1.523 | ort | 1.688 | |
| | | | | 611 | 1.486 | 1.484 | 320 | 1.466 | 1.469 | ort | 1.607 | |
| | | | | 041 | 1.238 | 1.242 | 150 | 1.349 | 1.350 | 301 | 1.550 | 1.547 |
| | | | | | | | 331 | 1.242 | 1.238 | ort | 1.524 | |
| | | | | | | | 400 | 1.214 | 1.213 | ort | 1.410 | |
| | | | | | | | | | | 103 | 1.365 | 1.366 |
| | | | | | | | | | | 203 | 1.207 | 1.233 |
| *a* (Å) | | | 4.93 | | | 9.79(3) | | | 4.85(1) | | | 4.98(1) |
| *b* (Å) | | | 5.07 | | | 5.13(1) | | | 7.03(2) | | | |
| *c* (Å) | | | 5.33 | | | 4.96(8) | | | 3.38(4) | | | 4.26(1) |
| *β* (°) | | | 97.3 | | | | | | | | | |
| $V/V_0$ | | | 0.953 | | | 0.899 | | | 0.833 | | | 0.763 |

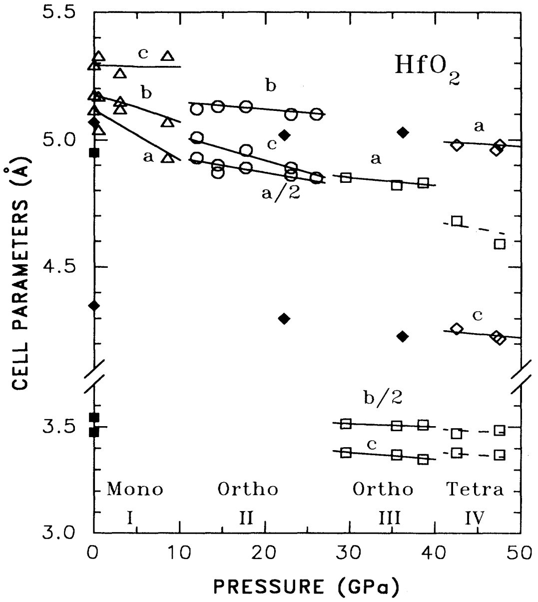

FIG. 2. Unit cell parameters of $HfO_2$ as a function of pressure. The symbols are the same as in Fig. 1. The monoclinic angle of phase I, not presented in this figure, decreases from 99.2° to 98° at 10 GPa.

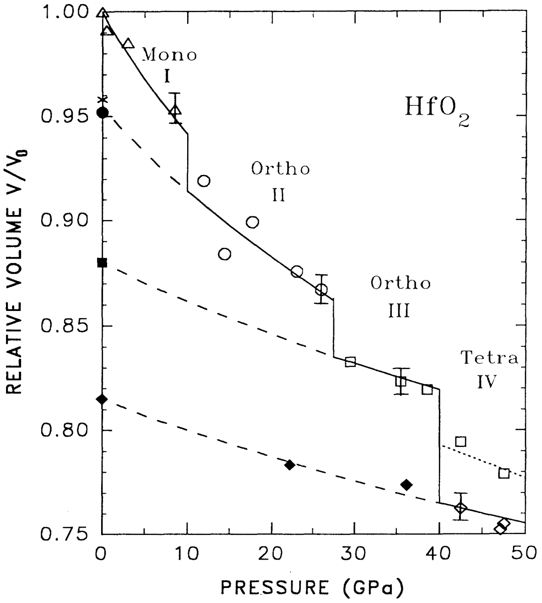

FIG. 3. Relative volume of $HfO_2$ as a function of pressure. The symbols are the same as in Fig. 1. The lines are from the fits to the Birch equation of state with the values of $B_0$ indicated in Table II.

sure (see below). The results are presented in Table II. The bulk modulus so obtained for monoclinic hafnia is equal to 145 GPa. The only experimental value (of about 460 GPa) which can be extracted from x-ray data under pressure to 20 GPa (Ref. 11) seems dubious: an apparent jump in the *a* parameter without any such discontinuity for the *b* and *c* parameters is actually obvious at 10–12 GPa, the solidification pressure of the 4:1 methanol-ethanol mixture used as pressure transmitting medium. Under these conditions, some discontinuities in the data and the presence of anisotropic stress components are very likely and thus could have produced a large amount of error in the measurements. A too high value of the bulk modulus would then be expected and this value (460 GPa) should be taken with caution.

The experimental value of the bulk modulus for the monoclinic phase I, 145 GPa, is lower than the value of 200 GPa expected from bulk modulus-volume systematics:[20]

$$B_0(\mathrm{GPa})=700S^2Z_AZ_C/V_0 \; .$$

In this relationship $V_0$ is the mean molar volume of an atomic pair, $S$ is the ionicity ($S^2=0.5$ for oxides), and $Z_C$ and $Z_A$ are the formal charges of the cation and anion, respectively. This observed reduction in $B_0$ shows that the monoclinic phase is possibly stabilized by symmetry breaking defects, but could also be due to the partial softening of an acoustic mode occurring prior to the martensitic shear transformation. A low bulk modulus was also measured for zirconia,[6] which is isostructural with $HfO_2$, and theoretical calculations[21] did not obtain the monoclinic phase as the stable phase at normal pressure.

The bulk modulus of the orthorhombic phase II of hafnia is equal to 210 GPa, which is exactly the value expected from the bulk modulus-volume systematics for this phase with such reduced volume ($V/V_0=0.955$). The large increase of the bulk modulus with respect to the monoclinic phase, $B_0=145$ GPa, confirms the unstable nature of the baddeleyite structure in these compounds. The bulk moduli of the other higher-pressure phases are considerably larger, and are about 475 and 550 GPa, respectively. Such high values are surprising; however, no large errors are expected ($\leq 15\%$) as the initial volumes were measured experimentally and the first pressure derivative was fixed to 5, its usual value. They cannot be explained either by the smaller volume of these phases, provided that the nature of the bonding remains the same. These values are close to that of diamond, a typical example of covalent bonding. The reason for this could be an increase in the covalent nature of the bonding under pressure; it should be pointed out that at normal pressure, partial covalent bonding was already proposed to occur in zirconia.[22]

The volume variations of hafnia over the investigated pressure range are very large; the relative volume (Fig. 3) is reduced to 0.75 at 50 GPa. These variations come from the low bulk modulus of the first, monoclinic, phase (i.e., its high compressibility) and from the successive volume decreases at the different phase transitions of about 2.5%, 2.5%, and 5%, respectively. Such a large overall volume change was not expected in such a refractory compound.

TABLE II. Bulk modulus and initial relative volume of the different phases of $HfO_2$ (the first pressure derivative of the bulk modulus was fixed to 5 and the initial volume at normal pressure was obtained from the recovered sample where all the phases were mixed together; the uncertainties are estimated to be ±1% for the relative volume of the high-pressure phase and 10–15 % for the bulk modulus under the above specified conditions).

| Phase | I<br>mono | II<br>ortho | III<br>ortho | IV<br>tetra |
|---|---|---|---|---|
| $(V/V_0)_{P=0}$ | 1 | 0.955 | 0.881 | 0.815 |
| $B_0$ (GPa) | 145 | 210 | 475 | 550 |

### Symmetry of high-pressure phases

For the normal-pressure phase which is stable up to 10 GPa, our data are in agreement with literature data; its monoclinic structure ($P2_1/c$, No. 14) was solved and refined several times at normal pressure.[11–13]

The data obtained for the high-pressure phase II (between 10 and 26 GPa) agree well with the orthorhombic structure shown in Ref. 9 to have the space group *Pbca* (No. 61). This is also, as is the monoclinic phase, a slight deformation of the parent fluorite-type phase with cubic symmetry (observed at high temperatures). Both structures, I and II, are the same as those occurring for $ZrO_2$. However, the similarity between hafnia and zirconia at high pressures is limited to these phases. The other high-pressure phases are different for both compounds.[6]

Above 26 GPa the small changes in the positions of several diffraction lines point to a new phase III with a totally different indexation within a new orthorhombic unit cell. The corresponding lattice parameters are close to 5, 7, and 3 Å, respectively (for details see Table I and Fig. 2). This is not the same phase as orthorhombic II in $ZrO_2$ existing over a similar pressure range. The unit cell of phase III is related to that of phase II by the following relations between lattice vectors: $\mathbf{a}_{\mathrm{III}}=\frac{1}{2}\mathbf{a}_{\mathrm{II}}$, $\mathbf{b}_{\mathrm{III}}=\mathbf{b}_{\mathrm{II}}+\mathbf{c}_{\mathrm{II}}$, and $\mathbf{c}_{\mathrm{III}}=\frac{1}{2}(\mathbf{b}_{\mathrm{II}}+\mathbf{c}_{\mathrm{II}})$. As the intensities of all lines are not determined accurately, there is no possibility of obtaining the positions of the atoms in the unit cell and, consequently, the space group of phase III. However, several space groups can be proposed from the partially known extinction rules, e.g., $Pbc2_1$ (No. 29), *Pbcm* (No. 57), $P22_12_1$ (No. 18), $Pnm2_1$ (No. 31), and *Pnmm* (No. 59). Moreover, this phase can be retained at normal pressure.

Above about 40 GPa six distinct new lines appeared, signaling the transition to phase IV. There are, however, nine other lines which can be considered to be lines from the previous phase III. Within this simplest assumption, there are no other lines which can be attributed to this highest-pressure phase; the newly observed diffraction lines can be indexed based on a tetragonal cell (see Table I). This tetragonal cell is related to the cell of phase III by the relations $\mathbf{a}_{\mathrm{IV}}=\frac{3}{2}\mathbf{c}_{\mathrm{III}}$ and $\mathbf{c}_{\mathrm{IV}}=\frac{1}{2}(\mathbf{a}_{\mathrm{III}}+\mathbf{b}_{\mathrm{III}})$. It is interesting to note that $c_{\mathrm{IV}}$ is thus equal to half of the body diagonal of the original monoclinic cell (or fluorite-type cubic cell of high-temperature phase). A detailed structure analysis is necessary to determine the real symmetry and space group of phase IV in $HfO_2$. It may be proposed, however, based on a few extinction rules, that the space group is one of $P4_22_12$ (No. 94), $P42_12$ (No. 90), $P\bar{4}2_1m$ (No. 113), or even $P4/n$ (No. 85), $P4_2/n$ (No. 86), and $P4/nmm$ (No. 129).

In the pressure range between 40 GPa and the highest pressure investigated, 47.5 GPa, the orthorhombic phase III coexisted with the tetragonal phase IV, but had a smaller volume than obtained by extrapolation (Fig. 3).

This tetragonal phase of $HfO_2$ has no similarities with the highest-pressure phase known for $ZrO_2$ around 50 GPa which was reported as being tetragonal[23] but is actually orthorhombic.[6] With the present tetragonal cell, only one line 110 out of the other nine lines observed for $ZrO_2$ in this pressure range could be indexed. The search for a common structure for both compounds in this pressure range was unsuccessful.

### Recovered sample at normal pressure

Upon decreasing the pressure from 47.5 GPa, the line 111 from phase IV was still observed at 10 GPa and lines from phases II and III were detected. Finally, after unloading, the sample was recovered from the pressure cell and a diffraction pattern was recorded under normal conditions with a standard Debye camera. The diffraction lines from all the four phases found under high pressure were observed (Table III). Thus a partial back conversion to the lower-pressure phases took place in our experiments. No other phase, such as the cotunnite-type phase, could be detected. At normal pressure the relative volume, $(V/V_0)_{P=0}$, of the quenched phase III is equal to 0.952, which is in excellent agreement with the value obtained from quenching experiments at 6 GPa and temperatures close to 1000 K (0.958).[8,9,11] The relative volume of phases III and IV, which are also metastable at normal pressure, are equal to 0.88 and 0.80, respectively. The monoclinic phase I recovered at normal pressure has a relative volume close to one, 1.01, which is an indication of the experimental uncertainties when four phases are mixed together. The approximate relative quantities of phases I–IV can be deduced from the observed pattern as 1:3:3:2 (Table III).

### Orthorhombic phase of cotunnite $PbCl_2$ type

The cotunnite-, $PbCl_2$-type, structure was proposed[3] for the orthorhombic-II phase appearing in $ZrO_2$ at about 21 GPa at room temperature. In our experiments, the lattice parameters of all phases of $HfO_2$ are significantly different from those of $PbCl_2$-type crystals indicating the absence of such a high-pressure structure at room temperature. The cotunnite-type structure was proposed for a sample of $HfO_2$ recovered at normal pressure after quenching experiment from pressures greater than 20 GPa and temperatures above 1300 K.[2] However, these data could be considered as arising from a mixture of several phases as in our own experiment performed at room temperature (see Table III). Moreover, the line at $d=2.77$ Å, rather strong in the $PbCl_2$ structure ($I/I_0=0.6$), was not observed in Ref. 2, supporting the hypothesis of the absence of a $PbCl_2$-type structure in

TABLE III. Diffraction pattern of $HfO_2$ at ambient pressure after pressurization to 47.5 GPa. The *hkl* correspond to the diffraction lines from four phases of hafnia under high pressure (*: line of highest intensity in each phase). For comparison the diffraction pattern of the phase quenched from 20 GPa and 1270 K (Ref. 2) is given.

| Ref. 2 | | Present work | | Phases | | | |
|---|---|---|---|---|---|---|---|
| $d$ (Å) | $I/I_0$ | $d$ | $I/I_0$ | I | II | III | IV |
| | | 3.623 | 20 | 110 | | | |
| 3.25 | 5 | | | | | | |
| | | 3.129 | 35 | $11\bar{1}$* | | | |
| 2.950 | 40 | 2.959 | 100 | | | 120* | |
| | | 2.903 | 100 | | 211* | | |
| 2.790 | 100 | 2.810 | 70 | 111 | | | |
| | | 2.771 | 70 | | | | 111* |
| | | 2.614 | 40 | 002 | 020 | 111 | |
| 2.603 | 50 | 2.594 | 50 | 020 | | | |
| | | 2.532 | 30 | 200 | | | 200 |
| | | 2.504 | 40 | $10\bar{2}$ | 400 | | |
| | | 2.325 | 10 | 012 | 021 | | |
| 2.140 | 5 | 2.178 | 5 | $12\bar{1}$ | | | |
| | | 2.083 | 5 | | 212 | | |
| 2.025 | 40 | | | | | | |
| | | 2.002 | 10 | 211 | | | |
| | | 1.829 | 40 | 022 | | | 112 |
| 1.806 | 25 | 1.811 | 40 | 220 | | | |
| | | 1.771 | 15 | | | 040 | |
| (etc.) | | (etc.) | | | | | |

$HfO_2$. This does not rule out the existence of such a high-pressure phase at high temperatures.

## CONCLUSION

*In situ* powder x-ray diffraction experiments have been performed at room temperature up to 47.5 GPa on hafnium dioxide. The transition from the monoclinic to orthorhombic phase was observed to occur at about 10 GPa. Above 26 and 42 GPa two previously unknown phases, labeled, respectively, as phases III and IV (do not confuse them with the orthorhombic-II and -III phases in $ZrO_2$), were discovered. Phase III is orthorhombic, while the symmetry of phase IV was tentatively assumed as tetragonal (however, a lower symmetry is always possible). No other orthorhombic phase, such as of cotunnite type reported from quenching experiments, could be detected in the present experiments. On releasing the pressure, the reverse transformations are incomplete and at normal pressure, the recovered sample consisted of a mixture of the four phases observed under pressure. The unit cell parameters and the volumes of the four high-pressure phases have been determined as a function of pressure. The bulk modulus of the monoclinic phase I is equal to 145 GPa. This value is smaller than expected from bulk modulus-volume systematics (for zirconia the corresponding monoclinic phase was calculated to be unstable at normal pressure). The bulk modulus of the orthorhombic phase II is equal to 210 GPa in agreement with the expected value from bulk modulus-volume systematics. Phases III (orthorhombic) and IV (tetragonal) have much higher bulk moduli, which could indicate enhanced covalent bonding. At higher pressures, the phase diagram of hafnia is different from that of zirconia although the two compounds have very similar properties at ambient and low pressures.

## ACKNOWLEDGMENTS

One of us (A.S.P.) would like to thank the CAPES, Brazilian Government Agency for financial support for the stay in France. P.E.T. would like to thank the French Ministry of Research and Technology for financial support. The Laboratoire de Physico-Chimie des Matériaux is Unité Propre No. 211 du CNRS.

---

[*] On leave from the Institute of Low Temperature and Structure Research, Polish Academy of Sciences, 50-950 Wroclaw, Poland.

[†] On leave from the Departamento de Materiais, Escola de Engenharia da Universidade Federal do Rio Grande do Sul, 90035-190 Porto Alegre, RS, Brazil.

[1] M. Ruhle and A. H. Heuer, in *Science and Technology of Zirconia II,* Advances in Ceramics Vol. 12, edited by N. Claussen (American Ceramic Society, Columbus, OH, 1984).

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

[3] S. Block, J. A. H. da Jornada, and G. J. Piermarini, J. Am. Ceram. Soc. **68**, 497 (1983).

[4] A. S. Pereira and J. A. H. da Jornada, J. Mater. Sci. Lett. **8**, 1353 (1989).

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

[6] J. M. Leger, P. E. Tomaszewski, A. Atouf, and A. S. Pereira, Phys. Rev. B **47**, 14 075 (1993).

[7] N. A. Bendeliani, S. V. Popova, and L. F. Vereshchagin, Geokhimiya **6**, 677 (1967).

[8] G. Bocquillon, C. Susse, and B. Vodar, Rev. Hautes Temp. Refract. **5**, 247 (1968).

[9] O. Ohtaka, T. Yamanaka, and S. Kume, Nippon Seramikkusu Kyokai Gakujutsu Ronbunshi **99**, 826 (1991) (in English).

[10] G. A. Kourouklis and E. Liarokapis, J. Am. Ceram. Soc. **74**, 520 (1991).

[11] D. M. Adams, S. Leonard, D. R. Russell, and R. J. Cernik, J. Phys. Chem. Solids **52**, 1181 (1991).

[12] R. Ruh and P. W. R. Corfield, J. Am. Ceram. Soc. **53**, 126 (1970).

[13] R. E. Hann, P. R. Suitch, and J. L. Pentecost, J. Am. Ceram. Soc. **68**, C-285 (1985).

[14] H. Arashi, J. Am. Ceram. Soc. **75**, 844 (1992).

[15] R. Suyama, H. Horiuchi, and S. Kume, Yogyo Kyokai Shi **95**, 567 (1987) (in English).

[16] I. Vedel, A. M. Redon, J. Rossat-Mignod, O. Vogt, and J. M. Leger, J. Phys. C **19**, 6297 (1986).

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

[18] DICVOL—program for indexing powder diagrams; D. Louer and M. Louer, J. Appl. Crystallogr. **5**, 271 (1972).

[19] F. Birch, Phys. Rev. **71**, 809 (1947).

[20] O. L. Anderson, in *The Nature of the Solid Earth,* edited by E. C. Robertson (McGraw-Hill, New York, 1972), p. 575.

[21] R. E. Cohen, M. J. Mehl, and L. L. Boyer, Physica B **150**, 1 (1988).

[22] S.-M. Ho, Mater. Sci. Eng. **54**, 23 (1982).

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