

Pressure-induced structural phase transitions in zirconia under high pressure

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Angular-dispersive x-ray *in situ* powder-diffraction experiments have been performed on pure zirconia, ZrO_2 , at room temperature under high pressure up to 50 GPa. Under increasing pressure four phases were successively encountered: baddeleyite (monoclinic, $P2_1/c$) from normal pressure up to about 10 GPa, orthorhombic-I ($Pbca$) to 25 GPa, orthorhombic-II to 42 GPa, and orthorhombic-III above 42 GPa. The unit-cell parameters and the volume have been determined as a function of pressure. The bulk moduli of the two lower pressure phases have been calculated using Birch's equation of state. The bulk modulus of baddeleyite, 95 GPa, is much lower than expected from bulk modulus-volume systematics, 195 GPa, while for the orthorhombic-I phase, the experimental and calculated values are almost identical. A generalized P - T diagram for ZrO_2 , including an orthorhombic-IV phase, is proposed and discussed. The phase transition to orthorhombic-II and orthorhombic-III phases can be described by a simple rotation of the unit cell of the orthorhombic-I phase about either the b axis to form the orthorhombic-II phase or a axis to form the orthorhombic-III phase. All high-pressure cells (orthorhombic-I, -II, and -III) have eight formula units ($Z=8$). The orthorhombic-II phase was found not to have the cotunnite $PbCl_2$ -type structure which was proposed previously. There is no longer any example of a compound which transforms to such a cotunnite-type structure under high pressure. The behavior of zirconia and hafnia under high pressure is different although they have very close chemical properties at ambient pressure and identical structures in the two lower-pressure phases.

I. INTRODUCTION

Zirconia, ZrO_2 , is a major component of modern ceramic materials that exhibit very interesting mechanical properties when the high-temperature tetragonal phase has been partially stabilized to produce the so-called tough hardening phenomena. Thus the crystal structure of zirconia polymorphs and the mechanisms of transitions between them are of considerable interest in view of their connection with the properties of advanced zirconia-based ceramics.

The high-pressure, high-temperature phase diagram of ZrO_2 has been extensively studied to determine the fields of stability of the different phases and bring some understanding to the mechanisms of the phase transitions, mainly the monoclinic-to-tetragonal one which is of martensitic nature. Moreover, the high-pressure behavior of zirconia can provide a useful analogy for the pressure-induced phase transitions in silica, which are important in relation to the study of the deep interior parts of the Earth.

The lack of reliable structural data on the high-pressure phases other than orthorhombic-I phase (with a correct space group of $Pbca$), motivated us to perform *in situ* measurements of the lattice parameters and determine the equations of state for the phases of ZrO_2 existing at room temperature. Thus, we have performed powder x-ray-diffraction experiments up to 50 GPa (500 kbar) on pure zirconia. Before proceeding to the description of the experimental procedure and results, it is useful to summarize some data about the structural properties.

The numerous data on pure and stabilized zirconia, which can be found in the literature, should be taken,

however, while paying special attention to several shortcomings or/and difficulties in the obtainment of meaningful experimental data and their correct interpretation. Therefore, we note the following.

(a) The use of x rays instead of neutrons, produce difficulties in the correct interpretation of the diffraction patterns of ZrO_2 due to small scattering factor from oxygen atoms (the x-ray-diffraction pattern could then be indexed based on an incorrect unit-cell symmetry as different positions of oxygen atoms might be indistinguishable). Attention should therefore be focused on neutron data.

(b) The diffraction pattern can be representative either of the bulk, as in x-ray or neutron diffraction, or the surface as in electron microscopy.

(c) The use of doped sample, e.g., stabilized ZrO_2 ceramics, can result in data which cannot be compared to data obtained from pure zirconia.

(d) The use of powdered samples does not provide direct information about the symmetry of the crystal studied.

(e) Measurements made on quenched samples far from thermodynamic equilibrium and without knowledge of the real history of the treated sample can result in an incorrect interpretation of the data (e.g., the case of a multiphases mixture).

(f) Conditions of the *in situ* measurements under pressure are extremely difficult.

Accordingly, the full crystal structure data where it exists should be considered first. The data on the lattice parameters alone or even with a more or less strictly determined space group, can result in an incorrect structure for the high-pressure phases.

A. Phase diagram of zirconia

Considering the conditions and restrictions on the interpretation of data mentioned above, we suggest the generalized pressure-temperature phase diagram for zirconia based on the literature¹⁻²³ in addition to this work.

Recent research has revealed the existence of several, at least seven, polymorphs of ZrO_2 which occur in different ranges of temperature and pressure. They are presented in Fig. 1. The stability fields of the different phases were determined either by *in situ* detection of phase transitions or by searching for different phases in samples quenched from different P - T conditions.

At ambient pressure, the crystal structures of ZrO_2 polymorphs (monoclinic, tetragonal, and cubic) were studied using neutron diffraction with considerable precision up to the highest temperatures.^{19,23-27} However, there are some controversies about the existence of an intermediate orthorhombic phase observed on heating only, and a possible second high-temperature tetragonal phase.^{19,21,28} Some crystal structure data are presented in Table I. The cubic ZrO_2 phase has the fluorite structure. Most of the other polymorphs, especially tetragonal and monoclinic, are derivatives of this structure. In a general description, these structures consist of layers of Zr atoms between two oxygen layers as in the amorphous form.^{29,30} Otherwise speaking, the structures are built from the fluorite structure by slight adjustments of the unit-cell parameters and by displacing oxygen atoms alternating above and below their ideal position in the (010) plane in cubic phase.^{21,31}

B. High-pressure phases

At higher pressure the situation is more complex as there are examples of contradictory data in the literature. Now, it seems obvious that all the high-pressure phases existing below 50 GPa and 1200 K are orthorhombic as is discussed below. However, only the structure of the high-pressure phase labeled as orthorhombic-I has been

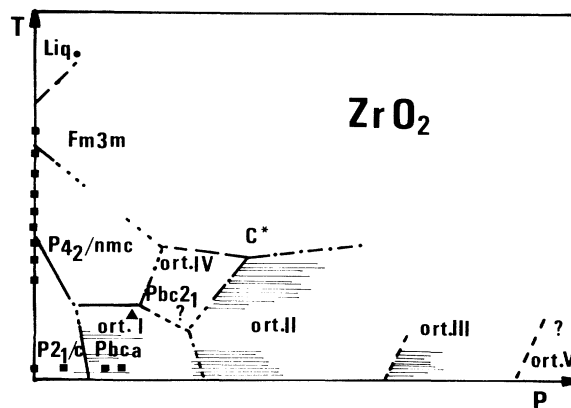


FIG. 1. Generalized pressure-temperature phase diagram for ZrO_2 . The stability fields of the different phases were determined either by *in situ* detection of phase transition (full lines in the diagram) or by search for different phases in samples quenched from different P - T conditions (dotted-dashed lines). Dashed lines correspond to those obtained from calculations and dotted lines are from our propositions. The hatched regions indicate the coexistence of phases or the uncertainties and/or inconsistencies of the data in the literature. The squares mark the full structure analysis made *in situ* and the triangle on quenched samples.

obtained by *in situ* crystal structure analysis;¹¹ two other structure refinements on this phase have been made on quenched samples.^{20,32} There are several other examples of orthorhombic symmetries for pure or partially stabilized ZrO_2 in different conditions.

The most controversial issues were concerning the phase labeled as orthorhombic-I (Ortho-I) which was first considered to be of tetragonal symmetry, but different from that observed at high temperature. After several years of extensive structure studies on different samples, one can firmly state that the correct space group of the

TABLE I. Literature data on space groups and lattice parameters for room- and high-temperature phases of ZrO_2 obtained by x-ray (X) or neutron (N) diffraction. The reliability factor R is also given for data from full structure determination on powder samples; only the data from Ref. 31 are from a single-crystal experiment (X_{mono}).

T (K)	Space group	a (Å)	b (Å)	c (Å)	β (deg)	N/X	R (%)	Ref.
2690	$Fm\bar{3}m$	5.230				X		a
		5.269				N		b
2440	$P4_2/nmc$	5.2022		5.3175		N		b
1900		5.1727		5.3048		N	8.6	c
1630		5.1458		5.2864		N	1.6	b
1100		5.1239		5.2413		N	6.45	c
1100	$P2_1/c$	5.1828	5.2117	5.3731	98.835	N	6.45	c
300		5.1495	5.2021	5.3198	99.238	N	8.35	c
300		5.145	5.2075	5.3107	99.233	X_{mono}	9.0	d

^aReference 21.

^bReference 26.

^cReference 23.

^dReference 31.

Ortho-I phase is *Pbca* (No. 61) with the unit-cell parameters of about 10–5–5 Å, respectively (twice *a* parameter with respect to the *Pbcm* (No. 57) disordered structure).²⁰ Selected data for this phase are presented in Table II. The crystal with the *Pbca* structure consists of a planar periodical arrangement of alternate obverse and reverse domains (more precisely: alternate types of an O1-atom net), leading to a doubling of the unit-cell parameter *a*.³³ These domains have a *Pbc2₁* (No. 29) symmetry and only one type of O1-atom net³⁴ is displaced from its position in the tetragonal high-temperature phase. Thus, this phase can be regarded as intermediate between the tetragonal and the monoclinic ones.³⁵ The average of domains of noncentrosymmetric *Pbc2₁* symmetry yields the centrosymmetric *Pbcm* (No. 57) structure model known from x-ray-diffraction data^{11,32} and not confirmed by neutron experiments.³³ In this structure the oxygen O(1) is disordered over the two sets of positions related by the mirror plane at $z = \frac{1}{4}$. It should be noticed that the coordination number does not change with respect to that in the monoclinic phase: It remains equal to seven. The proposed value of eight (Ref. 7) was based on the tetragonal high-pressure structure, which has been shown to be wrong.

The existence of the phase labeled as orthorhombic-II (Ortho-II) was determined by several studies. From quenching experiments the symmetry was assigned as *Pnma* (No. 62) and the cotunnite, PbCl_2 -type, structure was proposed.⁷ Some verification by powder refinement was reported on CaO-stabilized zirconia³⁶ but no details were given. The present experiment data on pure ZrO_2 under high pressure do not confirm this model.

Discussion of the orthorhombic-III (Ortho-III) phase is also included in this paper. Here it should be pointed out that the discovery of this phase above 35 GPa was previously discussed in terms of a tetragonal symmetry.¹⁸

The phase boundaries obtained from the different experiments and those added based on thermodynamic criteria provide evidence for the existence of a *P-T* field for a new phase labeled here as orthorhombic-IV (Ortho-IV). Actually, quenching experiments from these *P-T* conditions indicated an orthorhombic symmetry for this phase; however, the exact symmetry was not directly proved under high-pressure, high-temperature conditions. Both space groups proposed, *P2₁2₁2₁* (No. 19) (Ref. 3) and *Pbca* (No. 61) (Ref. 20), should be rejected: the first one was already rejected because of the too few Raman lines observed under pressure⁸ and the second corresponds to the Ortho-I phase. A possible solution within orthorhombic symmetry is to propose the space group *Pbc2₁* (No. 29) as was already found in electron-diffraction experiments for thin-foil specimens of stabilized zirconia^{37–41} and known as the symmetry of the domains which form the Ortho-I phase.³⁴

There are also some indications of a further phase transition at pressures higher than 55 GPa to a phase of a symmetry which is probably higher than orthorhombic.¹⁶ [The proposed cubic symmetry may be due, in our opinion, to a misinterpretation of the x-ray-diffraction lines which come mostly from the zirconium framework. Actually, if the framework of the oxygen atoms is also considered, then the highest possible symmetry should be orthorhombic *Pmmm* (No. 47) in order to retain the same structural motif. The lattice parameters would then be of about 2.5 Å with the oxygen atoms in the 1(*a*) and 1(*d*) positions, while Zr atoms occupy 2(*r*) positions with a probability of 0.5.

In the high-temperature, high-pressure region of the *P-T* diagram, the phase labeled as *C** (Ref. 17) seems to be the same as the well-known high-temperature, ambient-pressure cubic phase, but no experimental confirmation of this has been performed.

TABLE II. Selected data for high-pressure Ortho-I phase of ZrO_2 (only Ref. 34 concerns a partially stabilized zirconia) from x-ray (*X*) and neutron (*N*) experiments made *in situ* (*s*) or on quenched samples (*q*). Pressure and temperature conditions are given in [GPa] or [K] units, respectively, (AP=ambient pressure, RT=room temperature).

Symm.	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)	<i>R_B</i> (%)	<i>X/N</i>	<i>P;T</i>	Ref.
<i>P2₁2₁2₁</i>	5.036	5.267	5.073	134.6		<i>X</i>	4.0;2070 <i>q</i>	a
<i>P2₁2₁2₁</i>	5.016	5.230	5.016	131.6		<i>X</i>	9.9;730 <i>s</i>	b
Tetr.	5.009	5.237	5.009	131.4		<i>X</i>	8.3;RT <i>s</i>	c
Tetr.	5.046	5.129	5.046	130.6		<i>X</i>	7.3;1270 <i>q</i>	d
Ortho.	5.042	5.257	5.092	135.0		<i>X</i>	6.0;870 <i>q</i>	e
<i>Pbcm</i>	5.005	5.235	5.051	132.3	3.4	<i>X</i>	3.9;RT <i>s</i>	f
<i>Pbcm</i>	4.992	5.229	5.046	131.7	4.5	<i>X</i>	5.1;RT <i>s</i>	f
<i>Pbcm</i>	5.036	5.255	5.086	134.6	5.0	<i>X</i>	6.0;870 <i>q</i>	g
<i>Pbc2₁</i>	5.068	5.260	5.077	135.3	2.1	<i>N</i>	AP;30 <i>q</i>	h
<i>Pbca</i>	10.086	5.262	5.091	270.2	3.9	<i>N</i>	6.0;870 <i>q</i>	i
Ortho.	5.047	5.303	5.207	139.4		<i>X</i>	AP;1370 <i>s</i>	j

^aReference 3.

^bReference 6.

^cReference 9.

^dReference 10.

^eReference 56.

^fReference 11.

^gReference 32.

^hReference 34.

ⁱReference 20.

^jReference 21.

II. EXPERIMENTAL PROCEDURE

The powder x-ray-diffraction experiments were performed at room temperature using a diamond-anvil cell of the lever-arm type with diamonds of 500- μm diameter flats. The zirconium oxide was a powder with a grain size below 1 μm and a stated purity better than 99.9%. The 4:1 methanol-ethanol mixture generally used as pressure transmitting medium introduces some discontinuities in the resulting data⁴² when it solidifies and becomes glassy at room temperature at around 10–12 GPa, so silicon oil was preferred. The mixture of silicon oil and sample was loaded in the 150- μm diameter hole drilled in a T301 gasket of initial thickness 250 μm , preintended to 100 μm . Some additional experiments were performed below 10 GPa with the 16:3:1 methanol-ethanol-water mixture to further study the monoclinic-orthorhombic-I phase transition. 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 (fit with an anisotropic stress component) although the two maxima of the doublet were always clearly seen. The powder x-ray-diffraction patterns were recorded on wet films using the molybdenum radiation from a fine focus tube. The filtering of the $K\beta$ radiation was made less effective than usual to shorten the exposures to about 24 h. A few additional experiments were performed with increased filtering to check for the possible presence of lines due to the $K\beta$ radiation. A wide slit in the seat of the rear diamond allowed for recording of the diffraction patterns up to about $2\theta = \pm 40^\circ$ on films placed on a cylin-

drical support, with a sample-to-film distance of 25.47 mm.⁴² The diameters of the Deybe rings were measured with a low magnification microscope. The diffraction lines, which possibly coincided with the lines from gasket (mainly iron), were omitted in the discussion of our data. Indexing of the powder diagrams was performed using the DICVOL program.⁴³ Only single diffraction lines were used for lattice parameters refinements.

The experimental data on the pressure dependence of the relative volume V/V_0 obtained with the increasing pressure were fitted to Birch's equation of state:⁴⁴

$$P = \left(\frac{3}{2}\right) B_0 x (1+x)^{5/2} (1+ax),$$

where $x = (V/V_0)^{-2/3} - 1$ and $a = (3/4)(B'_0 - 4)$. B is the bulk modulus and B' its first pressure derivative; the subscript zero refers to values at normal pressure.

After pressurization to 47.5 GPa, additional diffraction patterns were recorded when the pressure in the diamond-anvil cell was gradually decreased.

III. RESULTS AND DISCUSSION

All experimental data, i.e., d spacings calculated from the positions of diffraction lines on the x-ray films, lattice parameters, and relative volume, are plotted vs pressure in Figs. 2, 3, and 4, respectively; in addition, representative data for each phase are presented in Table III. Four pressure regions are clearly seen which correspond to four different phases. Upon decreasing the pressure, an identical sequence of phase transitions was observed. All phase transitions were fully reversible and only some hysteresis was found. We could retain neither the orthorhombic-III phase down to normal pressure, con-

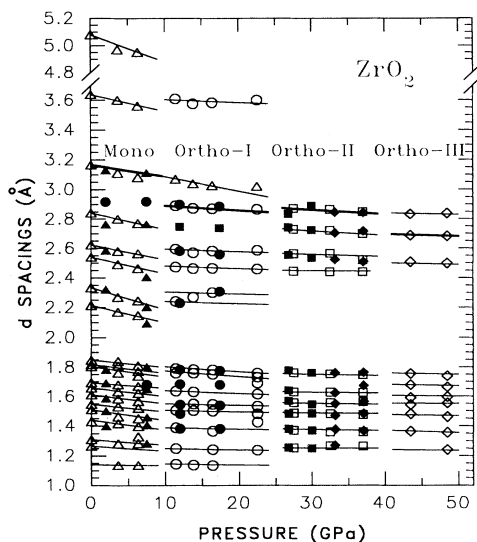


FIG. 2. Pressure dependence of the d spacings d of ZrO_2 . Open symbols: increasing pressure, filled symbols: decreasing pressure; \triangle : monoclinic phase; \circ : orthorhombic-I phase; \square : orthorhombic-II phase, and \diamond : orthorhombic-III phase. The lines are there to guide the eye (for increasing pressure only); the thick line is for the highest intensity line in each phase. The diffraction lines which possibly coincided with the lines from gasket (mainly iron) were omitted in the figure.

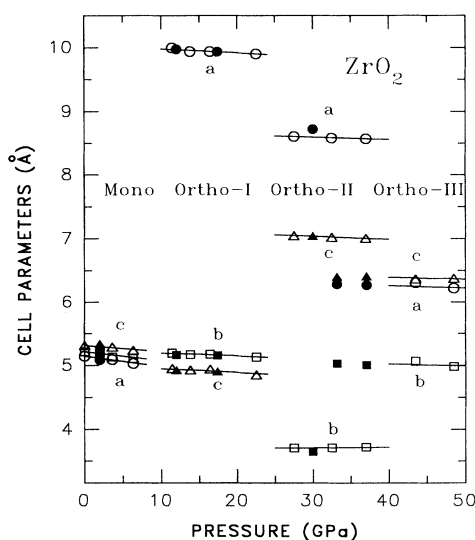


FIG. 3. Unit-cell parameters of ZrO_2 as a function of pressure. \circ : a parameter; \square : b parameter; \triangle : c parameter (open symbols: increasing pressure, filled symbols: decreasing pressure). With this choice of parameters, the structural motif can be conserved through all the crystallographic transitions. The lines are there to guide the eye. The monoclinic angle (99.8°) of the monoclinic phase does not vary significantly.

trary to the data reported in Refs. 18 and 45, perhaps due to the gradual decrease of the pressure in our experiments.

A. The baddeleyite monoclinic phase

Twenty one diffraction lines were observed in our experiments under pressure. The strongest line 111 was still observed at 22 GPa, while the other lines disappeared below about 10 GPa. The cell parameters are in good agreement with the values obtained at 3.9 and 5.1 GPa from single-crystal x-ray diffraction.¹¹ The pressure

variations of the unit-cell volume allowed us to calculate the bulk modulus: $B_0 = 95 \pm 8$ GPa for usual values, 4–5, of the first pressure derivative of the bulk modulus (as the pressure range of stability of the monoclinic phase is narrow, the exact value of B'_0 does not influence the value of the bulk modulus). This is smaller than a value of 135 GPa deduced from the shear and elasticity moduli of polycrystalline samples measured under normal conditions and extrapolated to zero porosity.⁴⁶ Recent Brillouin scattering experiments⁴⁷ at normal pressure performed on single crystals gave a mean value of 185 GPa, but these measurements could have been perturbed by

TABLE III. Interplanar distances (observed and calculated in first and second columns, respectively) with their indices and unit-cell parameters for each phase of ZrO_2 under high pressure (*: line of highest intensity; *m*: line from the monoclinic phase; -: line observed under other pressure; *Z*: formula units in the unit cell).

Phase <i>P</i> (GPa) (Å)	Mono 3.6		Ortho-I 16.4		Ortho-II 27.5		Ortho-III 48.5				
	d_{obs}	d_{cal}	d_{obs}	d_{cal}	d_{obs}	d_{cal}	d_{obs}	d_{cal}			
100	4.967	5.014	210	3.582	3.583	300	2.871*	2.869	102	2.837	2.836
011	3.60	3.656	<i>m</i>	3.026		202	2.729	2.726	012	2.681*	2.685
110	–	3.586									
11 $\bar{1}$	3.116*	3.139	211	2.871*	2.900	012	2.563	2.553	020	2.498	2.490
									112	–	2.466
111	2.802	2.798	020	2.583	2.585	112	2.448	2.448	302	1.738	1.738
002	2.577	2.606	400	2.464	2.484	004	1.761	1.761	222	1.663	1.659
020		2.565	002		2.470						
200	2.493	2.507	021	2.302	2.290	204	1.630	1.630	004	1.595	1.594
021	2.226	2.301	410	2.230	2.239	320	1.556	1.557	104	1.552	1.544
			121		2.232						
21 $\bar{1}$	2.175	2.195	420	1.782	1.791	214	1.490	1.492	114	1.470	1.475
102		2.164	022		1.786						
12 $\bar{1}$		2.154	402	1.753	1.752	404	1.368	1.363	214	1.360	1.364
022	1.846	1.827	421	1.690	1.684	612	1.253	1.251	040	1.246	1.245
220	1.807	1.793	230	1.630	1.629	603	1.224	1.224			
12 $\bar{2}$		1.788									
221	1.766	1.763	231	1.546	1.547						
202	1.680	1.669	611	1.500	1.052						
			213		1.496						
11 $\bar{3}$	1.632	1.644	422	–	1.450						
221		1.635	023	1.380	1.389						
31 $\bar{1}$	1.583	1.594	413	–	1.326						
13 $\bar{1}$		1.570									
22 $\bar{2}$		1.570									
30 $\bar{2}$	1.530	1.531	041	1.242	1.251						
131		1.522	800		1.242						
311	1.463	1.455	613	1.130	1.139						
13 $\bar{2}$	1.417	1.410									
222	1.396	1.399									
132	1.333	1.342									
040	1.282	1.282									
213		1.283									
331	1.136	1.135									
<i>a</i> (Å)		5.09			9.94(2)			8.607(19)			6.22(3)
<i>b</i> (Å)		5.13			5.17(1)			3.707(6)			4.98(4)
<i>c</i> (Å)		5.29			4.94(3)			7.044(5)			6.38(2)
β (deg)		99.89									
<i>V</i> (Å ³)		135.98			253.78			224.72			197.42
<i>V/V</i> ₀		0.966			0.902			0.798			0.701
<i>Z</i>		4			8			8			8

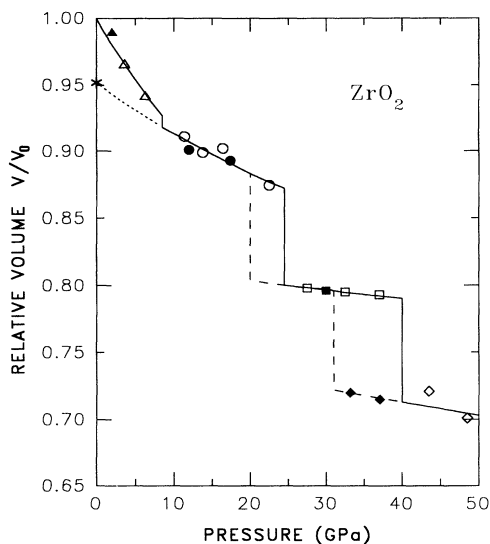


FIG. 4. Relative volume of ZrO_2 as a function of pressure. The graphic symbols are the same as in Fig. 2. The lines are there to guide the eye; dashed line: decreasing pressure, dotted line: fit of the data of the orthorhombic-I phase to the Birch equation using the volume under ambient condition obtained from quenched samples (20,34).

twinning as large crystals of the monoclinic phase are extremely difficult to make. From shock-wave data, the bulk modulus was inferred to be 149 GPa.⁴⁸

The experimental bulk modulus is much lower than expected (195 GPa) from bulk modulus-volume systematics:

$$B_0[\text{GPa}] = 700S^2Z_A Z_C / V_0,$$

where V_0 is the mean molar volume of an atomic pair, S the ionicity ($S^2=0.5$ for oxides), and Z_A and Z_C the formal charges of the anion and cation, respectively.⁴⁹ The experimental polyhedral bulk modulus can be calculated from previous data.¹¹ It is equal to 110 GPa and close to the volume bulk modulus. This indicates that there is no polyhedral tilting, as expected for a structure which is only slightly deformed with respect to the parent fluorite structure. Furthermore, no increase of the distortion of the unit cell with pressure could be evidenced. This experimental value is much lower than the value, 300 GPa, deduced from the polyhedral bulk modulus—versus the cation-anion distance relationship:⁵⁰

$$B_p = 750S^2Z_A Z_C / d^3,$$

where d (\AA) is the mean cation-anion distance. The lower experimental values for the volume bulk modulus and the polyhedral bulk modulus show that the monoclinic phase is possibly stabilized by symmetry-breaking defects. It could also arise from the partial softening of an acoustic mode occurring prior to the martensitic shear transformation. This is in good agreement with the results of the calculation within the potential-induced breathing model. Using this model, equations of state, relative phase stabilities, and elasticity of several different

structures of ZrO_2 were calculated.⁵¹ Interestingly enough, the monoclinic structure was found not to be the stable phase at ambient pressure. A monoclinic structure with a bulk modulus equal to 152 GPa was found to be stable, but at lower density than under ambient conditions. At higher densities, orthorhombic phases of ZrO_2 were found to be stable with bulk moduli of 273 and 314 GPa, respectively.

B. The orthorhombic-I phase

Between 8 and 11 GPa a phase transition was observed to take place in both silicon oil and liquid medium in general agreement with the literature data. Furthermore, shearing experiment on zirconia failed to detect this transition to 5 GPa. It is well known that this transition is sensitive to the grain size; in a single crystal it occurs at much lower pressure, 3.6 GPa.⁵² On releasing the pressure the most intense line can be seen down to 3 GPa.

Seventeen diffraction lines from this phase were observed. They could be indexed under orthorhombic symmetry and their intensities were in agreement with the proposed $Pbca$ (No. 61) structure model. The bulk modulus of the orthorhombic-I phase was calculated using the volume $V/V_0|_{p=0}=0.952$, the average value from the neutron² and x-ray-diffraction data,³⁴ both on a quenched sample. The first pressure derivative, B'_0 , was assumed to have the usual value of 5. The resulting bulk modulus is about 220 GPa and close to the expected one from the bulk modulus-volume relationship, 205 GPa. The volume change at the monoclinic to orthorhombic-I transition (0.8%) was smaller than the value obtained from the single-crystal study under hydrostatic pressure (3%).¹¹ It is evidence that the large difference in bulk moduli for the two phases induces a reduction in the volume decrease when the transition is shifted to higher pressures, as in this case.

C. The orthorhombic-II phase

The phase transition to the orthorhombic-II phase occurred between 22 and 27 GPa. The transition pressure was higher than reported in Ref. 9, because it was also sluggish, as was the lower-pressure one. On releasing the pressure the diffraction lines of this phase appeared at about 32 GPa and persisted down to 11 GPa (in coexistence with the lines of orthorhombic-I phase below about 20 GPa).

All 11 diffraction lines could easily be indexed on an orthorhombic cell with lattice parameters of about 8.6, 3.7, and 3.5 \AA . The molar volume decreased by 7.1% at this transition.

The cotunnite, $PbCl_2$ -type, structure was proposed for this phase.^{7,36} However, the line at about 2.45 \AA , which was observed *in situ* in our experiment and in Ref. 18, is forbidden in this structure. Thus, such structure model should be rejected. Furthermore, as far as the intensities of the diffraction lines are concerned, it is obvious that this line cannot be interpreted as the 002 line from the lower-pressure orthorhombic-I phase; the line 402 of similar intensity already vanished at about 18 GPa.

Moreover, the pressure dependence of the position of the lines of highest intensity in both phases (211 for orthorhombic-I and 300 for orthorhombic-II) displayed a noticeable discontinuity at the transition indicating the absence of the orthorhombic-I phase for pressures higher than 25 GPa. Thus, our *in situ* measurements did not confirm the existence of PbCl₂-type structure in ZrO₂ at room temperature under high pressure.

There is still further evidence for rejecting the PbCl₂-type structure as a structure model for the orthorhombic-II phase. At ambient pressure, although in Ref. 7 or in Ref. 36 there is no report of this line at about 2.45 Å on quenched samples, the intensities of other x-ray-diffraction lines are not in good agreement with the calculated values for a PbCl₂-type structure. Mainly, one characteristic and intense line of the proposed cotunnite structure at $d = 2.78 \text{ \AA}$ ($I/I_0 = 48$) was not reported; under normal conditions it should be well separated from the line at 2.80 Å ($I/I_0 = 96$). Moreover, it was not clear if additional lines (e.g., from the monoclinic phase) to the lines given in the paper⁷ were excluded from the published data or not. In the last case, the reported diagram could be explained by a mixture of several phases: monoclinic, orthorhombic-I and -II, as is the case for HfO₂.⁵³ Furthermore, the transition from the orthorhombic-I phase to a PbCl₂-type phase could require a great mutual displacement of both, zirconium and oxygen, sublattices. After the transition, both type of atoms would lie in the same planes; this seems to be unreasonable and questionable.

The nonexistence of the PbCl₂-type structure at high pressure, at least at room temperature, is of great importance because it leads to changes in the well-known diagram of the molar volume of MO₂ compounds vs the third power of the M-O distance.^{45,54} The proposed cotunnite-type high-pressure phase has no instances: There are neither ZrO₂ (this work) nor HfO₂ (Ref. 53) phases of this structure type at room-temperature high-pressure conditions.

It seems to be reasonable to retain the same general structure motif for zirconia in this phase. The similar conservation of the motif was observed in the phase transition from the monoclinic to orthorhombic-I phase. This led us to double the unit cell with respect to that found from our x-ray-diffraction data. Unfortunately, it is not possible to determine here which cell parameter, b or c , should be doubled. This cell doubling is not possible to detect in our experiments because of the small scattering factor of the oxygen atoms. For simplicity of the description only, especially in Table III, we chose to double the c axis. Within this model the phase transition from orthorhombic-I to orthorhombic-II phase is described as a rotation about the a axis providing to the following relations between unit cells: $\mathbf{a}_2 = \mathbf{a}_1$, $\mathbf{b}_2 = (1/2)(\mathbf{b}_1 + \mathbf{c}_1)$, $\mathbf{c}_2 = \mathbf{b}_1 - \mathbf{c}_1$. The preliminary powder diagram simulation using such model gives satisfactory agreement between observed and calculated line intensities. Unfortunately, the deduction of possible space group(s) is not possible.

The bulk modulus and the initial volume of the orthorhombic-II phase could not be calculated reliably

because this phase could not be retained down to ambient pressure in our experiment. Nor the value $(V/V_0)|_{P=0}$ given in the literature⁷ could be used, as it corresponds to another unit cell and no value could be derived for the orthorhombic-II cell.

D. The orthorhombic-III phase

A third pressure-induced phase transition in zirconia occurred between 37.5 and 42.5 GPa. It was mainly manifested by the appearance of two diffraction lines at about 2.500 and 1.675 Å. Upon decompression, this phase disappeared at about 32 GPa.

The ten observed diffraction lines could be indexed with a previously unknown, orthorhombic cell labeled as orthorhombic-III. In order to retain the same general motif for the ZrO₂ structure, as in the lower pressure phase, it was necessary to double the c axis (note, that the oxygen sublattice is not visible in our x-ray experiment). The search for simplest relations between the unit cells of orthorhombic-I and -III phases gave the following results: $\mathbf{a}_3 = (1/2)\mathbf{a}_1 + \mathbf{c}_1$, $\mathbf{b}_3 = \mathbf{b}_1$, $\mathbf{c}_3 = (1/2)\mathbf{a}_1 - \mathbf{c}_1$. The orthorhombic-III phase is achieved by a simple rotation of the unit cell about the b axis (thus, different from that necessary for obtaining the orthorhombic-II phase). The number of formula units is conserved ($Z = 8$) and the change of volume in the transition is about 7.7%. The simulation of the powder diagram within this model gave very satisfactory agreement of both calculated and observed intensities of diffraction lines.

This orthorhombic lattice also accounted for at least three of the four different lines observed in Ref. 18, where a tetragonal symmetry was assumed for this phase (the fourth line is close to a diffraction line from the gasket and was not considered here). From these four lines,¹⁸ it was not possible to calculate the lattice parameters of the orthorhombic unit cell proposed here. Thus, the volume of the previous tetragonal cell at normal pressure, where we could not retain this orthorhombic cell in a metastable state, could not be used for calculation of the volume variation with pressure. As a result the evaluation of the bulk modulus for the orthorhombic-III phase was not possible.

It should be pointed out that the general structural motif of ZrO₂ can be retained in all the high-pressure phases and thus, that the coordination number retains its original value of 7. The increase of the coordination number proposed in the literature⁷ from 7 to 8 and 9 has to be rejected as it was based on incorrect structures for the orthorhombic-I and orthorhombic-II phases.

The determination of the structures of post-baddeleyite phases is not as straightforward as previously anticipated. From the well-known structure map of AX₂ compounds it was thought that such phases would have fluorite- or cotunnite-type structures.⁵⁵ Now it is revealed that the cotunnite structure is not found, at least at room temperature up to pressures of 50 GPa and that many different structures can actually be observed: an orthorhombic cell in ZrO₂ with $Z = 8$, other orthorhombic and tetragonal cells with $Z = 4$ in HfO₂. This points out the necessi-

ty for further more detailed studies to be performed *in situ*.

IV. CONCLUSION

X-ray *in situ* powder-diffraction studies have been performed at room temperature on pure zirconia in a diamond-anvil cell using the angular-dispersive method. Under increasing pressure up to about 50 GPa, four phases were successively encountered: the ambient-pressure monoclinic phase (baddeleyite) and three orthorhombic phases. The unit cells of the two higher-pressure phases did not correspond to those previously reported: Neither the orthorhombic, cotunnite PbCl_2 -type structure nor the tetragonal phase were confirmed. The cotunnite structure previously proposed, mainly by referring to the structure map of AX_2 compounds, had to be rejected as one forbidden line was distinctly observed under pressure and one other characteristic intense line had not been reported in the earlier studies. The previously reported tetragonal structure, based on the analysis of only four diffraction lines, was also rejected; we could observe many additional lines and thus an orthorhombic cell was proposed. Although the diffraction patterns were of much higher quality in our experiment than previously reported, the correct space group of orthorhombic-II and -III phases in ZrO_2 could not be determined. Nevertheless, some structure models might be proposed from the observed relations between the unit cells of the different phases. The structural motif of ZrO_2 can be conserved through all the crystallographic transitions and thus, there is no evidence for an increase of the coordination number at room temperature up to 50 GPa. Further detailed crystal structure analyses are in progress now.

The unit-cell parameters and the volumes of the different phases have been determined over the whole pressure range of investigation. The bulk moduli of the two lower-pressure phases have been calculated. The value corresponding to the baddeleyite phase is much lower than expected from bulk modulus-volume systematics. It showed that this monoclinic phase is possibly unstable as predicted theoretically. The bulk modulus of the orthorhombic-I phase is, on the other hand, in good agreement with those systematics.

Zirconia was always considered to be analogous to hafnia, HfO_2 as they both display the same structural and chemical properties at ambient pressure, and undergo a lower-pressure phase transition to the same orthorhombic structure. However, it is now clear that the phase diagram of hafnia is different from that of zirconia: The phases above 20 GPa are not the same for both compounds (orthorhombic phase III and tetragonal phase IV for hafnia and orthorhombic-II and -III phases for zirconia). The study of quenched samples to compare hafnia and zirconia is of dubious use as the back transformations do not proceed in the same way.

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