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High-pressure phases of ZrO_2: An *ab initio* constant-pressure study

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The high-pressure behavior of ZrO_2 is studied using an *ab initio* constant-pressure technique up to 140 GPa. Two high-pressure phases of ZrO_2 are predicted through constant-pressure simulations. ZrO_2 undergoes a first-order phase transformation from the baddeleyite structure to an orthorhombic structure with space group *Pbcm* at 35–40 GPa. The coordination number of Zr atoms unexpectedly changes from sevenfold to sixfold owing to this phase transformation. Further increase in pressure leads to another first-order phase transformation from the *Pbcm* structure to a tetragonal one with the space group $P4/nmm$ at 70–80 GPa. In this structure, Zr atoms are ninefold coordinated. These phase transformations should occur around 11 and 38 GPa from enthalpy calculations, respectively.

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I. INTRODUCTION

Zirconia (ZrO_2), an important ceramic, possesses very interesting mechanical properties. Therefore, its crystal structures and the mechanisms of transition between its phases are considerably interesting in view their connection with properties of advanced zirconia-based materials and the pressure-induced phase transitions in SiO_2 because ZrO_2 is expected to have analogous chemical and structural properties to SiO_2 (Refs. 1 and 2) and other potentially hard ceramics with important geophysical implications.[3] However, in spite of extensive research efforts,[4–16] there are still unknowns and controversies about its high-pressure behavior. Experiments bring more questions than the answer about its high-pressure phases and invalidate each others. The aim of this study is to shed some light onto pressure-induced phase transitions in ZrO_2 using a constant-pressure *ab initio* technique.

ZrO_2 crystallizes in a monoclinic baddeleyite structure ($P2_1/c$). At high pressures and temperatures, it shows ten different solid structures. Earlier x-ray-diffraction study reported that ZrO_2 transformed into an orthorhombic phase with space group *Pbcm* around 4 GPa.[4] Heuer *et al.*[5] also obtained this phase from the transition electron microscopic observation of a ZrO_2 thin film. This transformation however was not confirmed in later studies[6–9] and instead a phase transition into an orthorhombic state with space group *Pbca* was reported in those experiments. At higher pressures, the formation of another orthorhombic phase with space group *Pnma*, isostructural to the ninefold-coordinated cotunnite ($PbCl_2$) structure, was reported in several experiments.[10–12] Other experiments, on the other hand, questioned the formation of the cotunnite-type phase in ZrO_2. Léger *et al.*[7] showed three sequence phase transitions at room temperature, baddeleyite → orthorhombic-I(*Pbca*) → orthorhombic-II → orthorhombic-III, around 10, 25, and 42 GPa, respectively. The symmetry of orthorhombic-II and orthorhombic-III has not been identified yet to our knowledge. Arashi *et al.*[13] observed a phase transition at 13 GPa, but were not able to verify a cotunnite structure. Additionally, the authors found a quenchable tetragonal phase about 35 GPa (most likely space groups were $P4/m$, $P4_2/n$, $P4/mmm$, or $P4/mbm$). In addition to these structures, tetragonal (MnF_2) and hexagonal phases[12,14] were observed in experiments as well.

Analyzing experimental data for ZrO_2 is indeed quite difficult because experiments yielded contradictory observations. Several factors in these studies might limit obtaining meaningful data or correct interpretations for the high-pressure phases of ZrO_2.[6,7] The controversies might be associated with the misinterpretation of the diffraction patterns of ZrO_2 due to the small scattering factor from oxygen atoms. It is also possible that the sample properties might favor the formation of specific crystalline states in ZrO_2. The use of doped sample stabilized ZrO_2 sample can result in data that cannot be compared to data obtained from pure ZrO_2. The use of powdered samples does not provide direct information about the symmetry of the crystal studied. Furthermore, experimental conditions, in particular, loading conditions and the degree of hydrostatic compressions, might result in some of these crystalline states. The influence of these factors on pressure-induced phase transitions in ZrO_2 cannot be easily addressed experimentally and hence reliable simulations become very appealing to reveal its true high-pressure behavior. Here we study the pressure-induced phase transitions of an ideal pure ZrO_2 crystal under perfect hydrostatic condition using a constant-pressure *ab initio* technique and find the formation of two phases. Both phase transitions are first order. The baddeleyite structure transforms into an orthorhombic structure (*Pbcm*) at 35–40 GPa and this orthorhombic phase converts to a tetragonal one ($P4/nmm$) at 70–80 GPa. The baddeleyite-to-*Pbcm* phase transition is unusual that it is associated with a decrease in the coordination numbers.

II. COMPUTATIONAL METHOD

We used the first-principles pseudopotential method within density-functional theory and the generalized gradient approximation of Perdew *et al.*[17] for the exchange-correlation energy. The calculation was carried out with the *ab initio* program SIESTA (Ref. 18) using a linear combination of atomic orbitals as the basis set, and normconservative Troullier-Martins pseudopotentials.[19] A split-valence double-ξ plus polarized basis set was employed. A uniform mesh with a plane-wave cutoff of 150 Ry was used to represent the electron density, the local part of the pseudopotentials, and the Hartree and the exchange-correlation potential. The simulation cell consists of 96 atoms with periodic boundary conditions. We used Γ-point sampling for the Brillouin-zone integration. The system was first equilibrated at zero pressure, and then pressure was gradually increased by an increment of 10.0 GPa. For each value of the applied pressure, the structure was allowed to relax and find its equilibrium volume and lowest energy by optimizing its lattice vectors and atomic positions together until the stress tolerance was less than 0.5 GPa and the maximum atomic force was smaller than 0.01 eV Å^{-1}. For minimization of geometries, a variable–cell shape conjugate-gradient method under a constant pressure was used. For the energy-volume calculations, we considered the unit cell for ZrO_2 phases. The Brillouin-zone integration was performed with automatically generated $6\times6\times6$ k-point mesh for the phases following the convention of Monkhorst and Pack.[20] In order to determine symmetry of the high-pressure phases formed in the simulations, we used the KPLOT program[21] that provides detailed information about space group, cell parameters, and atomic position of a given structure. For the symmetry analysis we used 0.2 Å, 4°, and 0.7 Å tolerances for bond lengths, bond angles, and interplanar spacing, respectively.

TABLE I. The atomic fractional coordinates and the equilibrium lattice parameters of the *Pbcm* and *P*4/*nmm* phases.

Structure	*a* (Å)	*b* (Å)	*c* (Å)	*x*	*y*	*z*
Pbcm	5.017	5.319	5.073	Zr: 0.22917	0.53096	0.25
				O: 0.40496	0.88536	0.25
				O: 0.04686	0.25	0.0
*P*4/*nmm*	3.439	3.439	5.341	Zr: 0.25	0.25	0.2631
				O: 0.25	0.25	0.8795
				O: 0.75	0.25	0.5

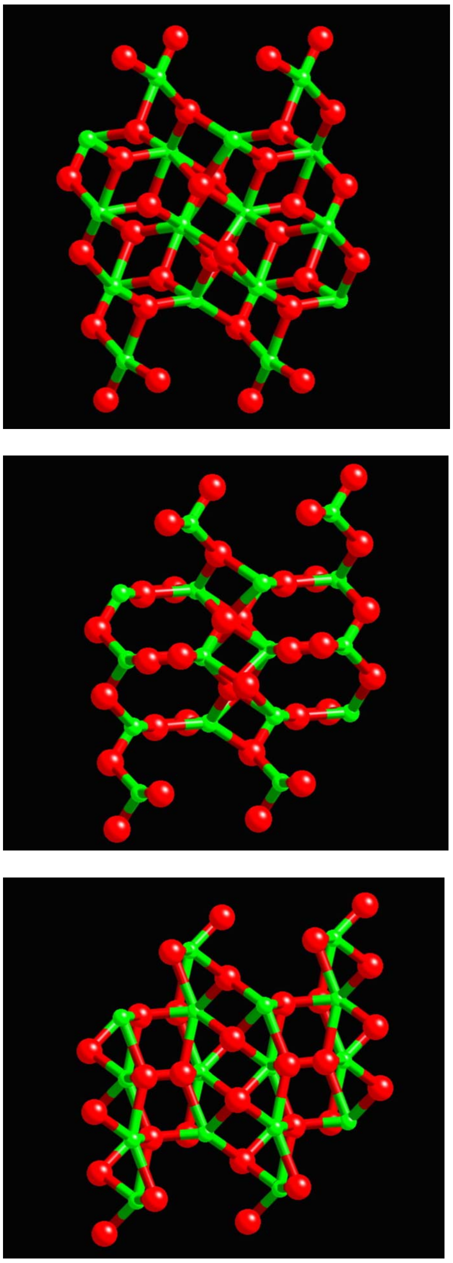

FIG. 1. (Color online) Crystal structures of ZrO_2: baddeleyite (top panel) at zero pressure, *Pbcm* (middle panel) at 40 GPa, and *P*4/*nmm* (bottom panel) at 80 GPa. All phases are viewed along [010] direction.

III. RESULTS

We analyze the structure of ZrO_2 at each applied pressure using the KPLOT program and find that the monoclinic symmetry ($P2_1/c$) is maintained up to 40 GPa. At this pressure we see the formation of an orthorhombic state with space group *Pbcm*. This crystal is illustrated in Fig. 1 and its structural parameters and the atomic positions are summarized in Table I. The *Pbcm* phase is unusual in that the Zr atoms are sixfold coordinated and the half of the O atoms is twofold coordinated. The interatomic distances and angles show the octahedron to be very distorted and the Zr-O bond lengths range from 1.99 to 2.22 Å. The oxygen atoms associated the longest Zr-O bonding are coordinated by two Zr atoms, whereas the others are coordinated by four Zr atoms. The O-Zr-O angles range from 77° to 145°. The second closest Zr-O distance is about 2.7 Å. A careful analysis indicates that the bonding between Zr atoms and threefold-coordinated O atoms in the baddeleyite structure is broken, resulting in a decrease in the coordination numbers owing to the phase transformation. Earlier x-ray-diffraction experiment[4] also reported the formation of an orthorhombic phase within *Pbcm* symmetry. However in that *Pbcm* structure, the coordination number does not change with respect to that in the baddeleyite phase. Therefore it is different from the one obtained the present work.

An ideal way to elucidate the mechanism of this phase change is to investigate directly the pressure dependence of the simulation cell vectors. Figure 2 shows the cell lengths and angles as functions of the applied pressure. As one can

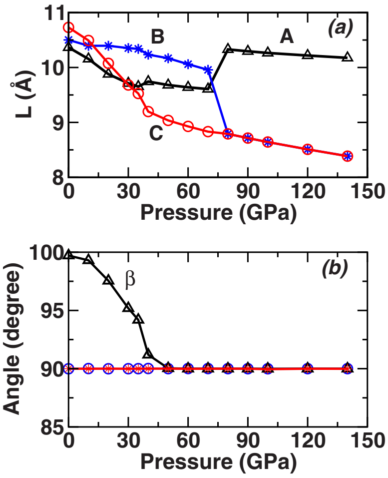

FIG. 2. (Color online) Changes in the simulation cell lengths and angles as functions of pressure. The simulation cell vectors **A**, **B**, and **C** are initially along the [100], [010], and [$\bar{1}$01] directions, respectively. The magnitudes of these vectors are plotted in the figure. The β is the angle between **A** and **C** vectors.

clearly see from the figure, the ZrO_2 structure exhibits a strong anisotropic compression. The c axis is found to be more compressible than the other axes. After 35 GPa, it shows a change in slope and the compression in this direction becomes slower. The monoclinic β angle gradually decreases and at 40 GPa it reaches a value of about 90°. Above this pressure this angle remains 90°. These observations lend further support for the occurrence of the phase transition in ZrO_2 at 40 GPa and suggest that the transformation mechanism of the baddeleyite-to-*Pbcm* phase change is very simple and can be easily pictured in terms of the modification of the monoclinic β angle and a dramatic compression along the c direction.

In order to determine the thermodynamic nature of the baddeleyite-to-*Pbcm* phase transition in ZrO_2, we plot the pressure-volume relation in Fig. 3. As can be seen from the figure, the volume decreases monotonically and shows a small discontinuity at 40 GPa, indicating a first-order phase transition.

In order to see how the *Pbcm* phase responds to the applied pressure, we pressurize it up to 140 GPa. As can be seen from the pressure-volume curve, another discontinuity occurs at 80 GPa, at which point a tetragonal structure with space group $P4/nmm$ is formed. This structure is illustrated in Fig. 1 and its parameters are given in Table I. The coordination configuration of the Zr atoms is 9, as in the cotunnite phase. This phase transformation is due to a dramatic compression along the b direction and an expansion along a direction as shown in Fig. 2. During the phase transformation, the simulation cell angles remain 90° and hence this phase change is not associated with any shear deformation.

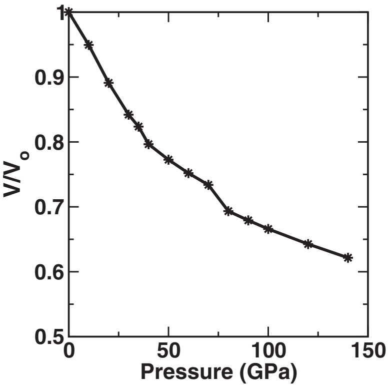

FIG. 3. Pressure-volume curve.

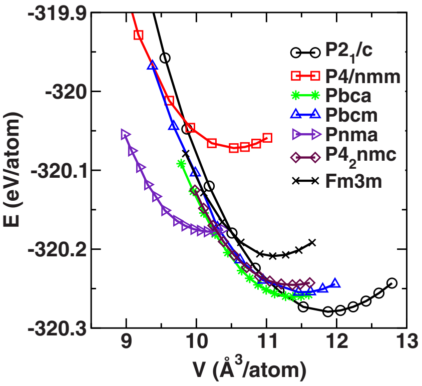

FIG. 4. (Color online) The computed energies of ZrO_2 phases as functions of volume.

Transition pressures predicted in constant-pressure simulations are generally overestimated, in analogous to superheating molecular-dynamics simulations. This implies a high intrinsic activation barrier for transforming one solid phase into another in simulations. When the particular conditions such as finite size of simulation cells and the lack of any defect in simulated structures are considered, such overestimated transition pressures are anticipated. Structural phase transformations in simulations do not proceed by nucleation and growth, but instead they occur across the entire simulation cells. As a result, systems have to cross a significant energy barrier to transform from one phase to another one, and hence simulated structures have to be overpressurized in order to obtain a phase transition.[22,23] Additionally the absence of thermal motion (relaxation of the structure at constant pressure) in our simulations shifts the transitions to

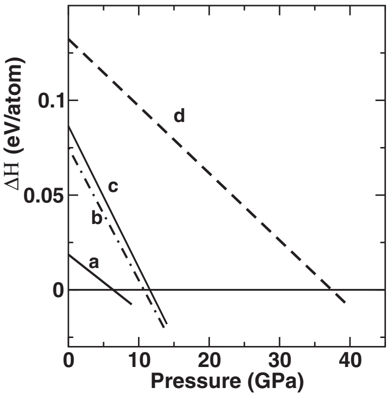

FIG. 5. The calculated enthalpies of ZrO_2 structures as functions of pressure: (a) $\Delta H = H_{\text{baddeleyite}} - H_{Pbca}$; (b) $\Delta H = H_{\text{baddeleyite}} - H_{Pbcm}$; (c) $\Delta H = H_{Pbca} - H_{Pnma}$; (d) $\Delta H = H_{Pbcm} - H_{P4/nmm}$.

higher pressures. On the other hand, the thermodynamic theorem does not take into account the possible existence of such an activation barrier separating the two structural phases and the thermal motion. Therefore as a next step, we consider the energy-volume calculations to study the stability of high-pressures phases of ZrO_2. The computed total energy-volume relations are fitted to the third-order Birch-Murnaghan equation of states and shown in Fig. 4. We also study the energy-volume relation of the known phases of ZrO_2 to compare the energetic of the phases predicted in this study with them. In Table II, we summarize the lattice parameters, bulk moduli, equilibrium volumes, and relative energy differences, with available experimental and theoretical results. As seen from the table, the present simulation technique produces comparable results with experiments and the previous plane-wave calculations.[6,8,9,15,16,24–26]

From the energy-volume data we calculate the static enthalpy, $H=E_{\mathrm{tot}}+PV$, because at zero temperature the thermodynamically stable phase is the one with the lowest enthalpy. The phase-transition pressures are evaluated by computing the enthalpy changes ΔH $(=H_i-H_j)$ at different pressures. Figure 5 shows the enthalpy changes ΔH as a function of pressure. The baddeleyite-to-*Pbcm* phase transition occurs around 11 GPa and the second phase change occurs near 38 GPa. Therefore, we expect to see these phase transitions around these pressures in experiments. The transition pressures between baddeleyite and *Pbca* and between *Pbca* and cotunnite phases are predicted to be 6.32 GPa and 11.26 GPa, respectively. These values are comparable with the theoretical results of 6.64–7.92 GPa (Refs. 16 and 24) and 9.2–12.15 GPa.[16,24] The enthalpy calculations also indicate that a phase transition from *Pnma* to $P4/nmm$ unlikely occurs be-

TABLE II. Equilibrium lattice parameters, volumes, relative energy differences, and the bulk moduli of ZrO_2 phases. All angles are 90° except for monoclinic β angle, which is 99.66°. References 6, 8, 9, and 26 are experimental results.

Structure	a (Å)	b (Å)	c (Å)	ΔE_0 (eV)	V_0 (Å^3)	B_0 (GPa)	Reference
$P2_1/c$	5.1676	5.2445	5.3342	0	35.62	138	This study
	5.1974	5.2798	5.3498	0	36.18	137	16
	5.19	5.25	5.35		36.0	218	24
	5.17	5.23	5.34	0	35.628	157	15
	5.08	5.20	5.22	0	34.158		25
	5.15	5.21	5.31		35.1		26
					35.16	212	8
Pbca	10.0837	5.2899	5.1189	0.019	34.13	227	This study
	10.1745	5.3148	5.1357	0.049	34.688	204	16
	10.015	5.29	5.12		34.4	230	24
	9.94	5.17	4.94	−0.033	31.733	272	15
	10.08	5.26	5.09		33.7		6
					33.49	243	8
$P4_2nmc$	3.6074		5.2420	0.034	34.10	172	This study
	3.6287		5.207	0.109	34.470	199	16
	3.61		5.25		34.2	226	24
	3.56		5.09		32.4		25
Fm3m	5.1080			0.07	33.33	242	This study
	5.1280			0.171	33.712	251	16
	5.11				33.4	236	24
	5.13			0.015	33.75	267	15
	5.03				31.9		25
	5.09				32.9		26
Pnma	5.5755	3.3517	6.5216	0.11	30.46	234	This study
	5.5530	3.3029	6.4842	0.26	30.859	251	16
	5.63	3.35	6.53		30.8	254	24
	5.71	3.25	6.34	−0.025	29.41	305	15
	5.58	3.32	6.48		30.1	332	9
					30.805	444	8
Pbcm	5.017	5.319	5.073	0.076	33.85	142	This study
$P4/nmm$	3.439	3.439	5.341	0.21	31.59	192	This study

cause their enthalpies are parallel to each other.

The cotunnite phase of ZrO_2 is promising as a new superhard material because of its high bulk modulus of about 320 GPa. Therefore it is interesting to study the bulk modulus of these two phases to see whether they possess the same hardness. The calculated bulk moduli are also given in Table II. Again our results are comparable with experimental and theoretical values except that the bulk modulus of cotunnite is quite less than the experimental results of 332 and 444 GPa. Our result for the cotunnite phase, on the other hand, agrees with the plane-wave calculations.

IV. DISCUSSION

Several experiments reported the baddeleyite → *Pbca* phase transformation around 10 GPa. Our energy-volume calculations also suggest that the formation of *Pbca* at high pressure is indeed thermodynamically more favorable than the *Pbcm* phase. We however do not observe a phase transformation into a *Pbca* crystal in the constant-pressure simulations. Different conditions of experiments and simulations might produce this contradictory observation:

(i) The sample properties might have some influence on pressure-induced phase transitions: the experimental samples are, in reality, not 100% pure and phase transformations nucleate and grow at defects, while the structure simulated is 100% pure and the phase changes proceed homogenously. Therefore using an ideal structure in the simulation might favor the formation of *Pbcm* phase rather than *Pbca*.

(ii) The different observation might be related to the degree of hydrostatic pressure, which is determined by the efficiency of the pressure-transmitting medium in experiments. At high pressures, the pressure-transmitting medium solidifies, resulting in strong nonhydrostatic effects. Even in the low-pressure regime, pressure in the diamond anvil cell is not exactly hydrostatic. In the simulations, on the other hand, the hydrostatic pressure is ideal. Thus, the different behavior might be a result of nonhydrostatic effects.

(iii) Temperature is also another factor that influences phase transformations. One might think that the lack of thermal effect might drive these phase transformations in the present work. If this is the case, then our simulations suggest that ZrO_2 might follow transformation mechanisms at low temperatures that are apparently different from ones observed at room temperature and high temperatures. New experimental studies performed at low temperatures are required to confirm these structural phase transformations (*Pbcm* and $P4/nmm$).

Currently we do not know which condition plays a predominant role for the different observations. It might even possible that one condition (sample properties, nonhydrostatic effect, and thermal effect) is not enough to produce the contradictory observations alone but their correlations determine the high-pressure phases of ZrO_2. Certainly further experimental and theoretical studies are needed to better understand the controversies reported in experiments and simulations.

V. CONCLUSIONS

Using a constant-pressure *ab initio* technique, we predict two high-pressure phases of ZrO_2. The coordination number of Zr atoms and the half of the O atoms are unexpectedly decreased owing to the baddeleyite-to-*Pbcm* phase transition. In the second phase transition we observe the formation of a tetragonal state with space group $P4/nmm$ in which the Zr atoms are ninefold coordinated. Both phases observed in our simulations do not correspond to any known ZrO_2 phases. At the present, however, we do not know whether previously proposed phases are a result of temperature, quenching, or nonhydrostatic effects. Therefore further studies at different temperature, loading rate, and nonhydrostatic conditions are desirable to reveal the pressure-temperature phase diagram of ZrO_2 and to explain the controversies reported by experiments.

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