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Relative stability of ZrO_2 and HfO_2 structural phases

J. E. Lowther and J. K. Dewhurst
Department of Physics, University of the Witwatersand, Johannesburg, South Africa

J. M. Leger and J. Haines
CNRS, Laboratoire de Physico-Chimie des Materiaux, 92190 Meudon, France

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The potentially hard oxides ZrO_2 and HfO_2 are investigated using *ab initio* electronic structure calculations and structural properties of the lowest phases compared. In general there are strong similarities between some phases apart from the softer monoclinic baddeyelite phase, which in HfO_2 is the lowest energy phase with a bulk modulus almost twice that of ZrO_2. Other differences relate to the formation of the first orthorhombic phase, especially the inter-relation between $Pbc21$ and $Pbca$ structures. The bulk moduli of the high-pressure, cotunnite-type phases are in good agreement with experimental results. The present calculations confirm that these phases are highly incompressible and are thus good candidates for hard materials.
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There is a considerable interest in the high-pressure phases of metal oxides.[1–10] These phases typically exhibit very high bulk moduli and thus are candidates for hard materials. Of the various metal oxides that have now been considered, ZrO_2 and HfO_2 are two reported to have potential superhard high-pressure phases,[1,5,11–16] and therefore hold potential as refractory materials. Very often the experimental pressure needed for inducing a phase transition depends upon many factors such as crystalline size or even material history or preparation, confusing an accurate characterization of the material. Thus an accurate experimental determination of elastic constants can be rather difficult and here computer modeling can play an important role in establishing properties of specific phases.

From the recent theoretical study of zirconia[17] it has been suggested that cotunnite may be the hardest phase of this material, at least as learned from the high value of the bulk modulus. This phase also has the highest oxygen coordination. The purpose of this paper is to compare properties of the most important phases of ZrO_2 with those of HfO_2. Although such materials are anticipated to be similar in that Zr and Hf belong to the same column of the Periodic Table, the calculations predict similar behavior in the order that the phases occur under pressure yet show small differences in energy suggesting that the routes of chemical synthesis could be subtly different.

We use the *ab initio* local-density approximation[18] (LDA) to obtain accurate exchange and correlation energies for a particular unit-cell configuration. Atoms in the unit cell were fully relaxed as was the overall cell structure. When possible, i.e., if the phase has been identified experimentally, known coordinates were used as a starting reference. A plane-wave basis with soft Troullier-Martins[19] pseudopotentials were used here with cutoff radii of Zr (2.64, 3.08, 2.34 a.u.) and Hf (2.54, 2.96, 2.25 a.u.) for the *s*, *p*, and *d* components, respectively. The pseudopotentials were checked for the presence of any ghost states. For O, cutoff radii of 1.45 a.u. were used for both the *s* and *p* channels. A criterion of at least 10^{-4} eV/atom was placed on the self-consistent convergence of the total energy and the calculations reported here used a plane-wave cutoff of 64 Ry.

The structure of the most important phases that we have considered are shown in Fig. 1. Such phases have quite a dense packing in the unit cell with orthorhombic-I ($Pbca$)

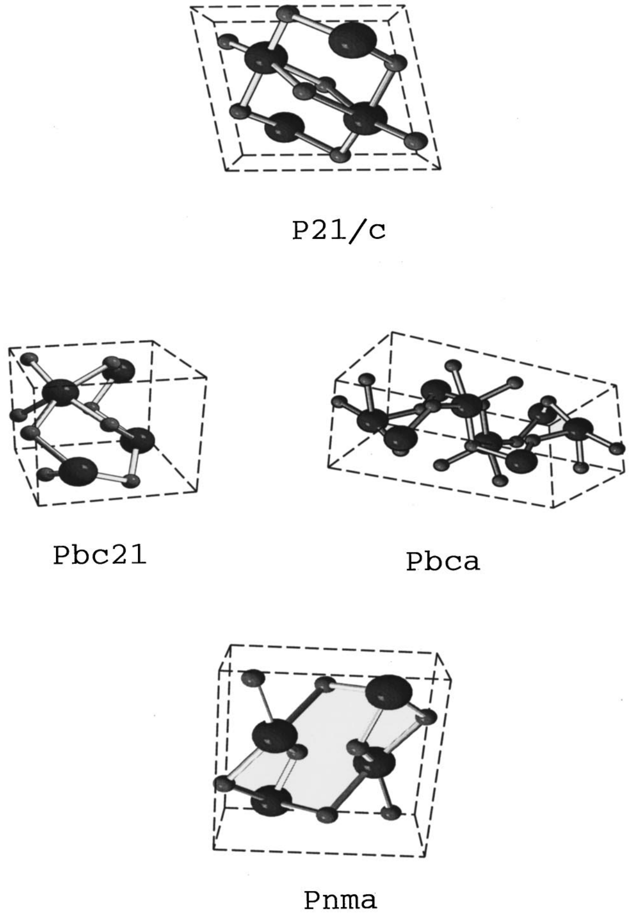

FIG. 1. Crystal structures of some important phases of ZrO_2 and HfO_2. Larger spheres represent the metal atoms.

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TABLE I. Calculated equation of state properties and relative energies of some phases ZrO_2 and HfO_2. Z is the number of atoms in the unit cell and C the average number of oxygens about Zr or Hf.

Phase	Z	C	ZrO_2			HfO_2		
			B (GPa)	B'	ΔE_0 (eV/atom)	B B (GPa)	B'	ΔE_0 (eV/atom)
Baddeleyite ($P2_1/c$)	4	7	157	2.38	0.000	251	4.40	0.000
$Pbc21$	4	7	264	4.62	-0.020	272	4.66	0.008
Fluorite ($Fm3m$)	4	8	267	4.42	0.015	280	4.63	0.056
Cubic ($Pa3$) 4		8	257	4.66	0.159	262	4.60	0.202
Orthorhombic-I ($Pbca$)	8	8	272	4.63	-0.033	256	4.15	0.020
Cotunnite ($Pnma$)	4	9	305	4.68	-0.025	306	4.57	0.020

being the largest cell containing 24 atoms. All the other unit cells contain 12 atoms. The monoclinic baddeleyite ($P21/c$) structure had the largest number of degrees of freedom—with the unit cell being specified by three cell vectors and an angle β. We held the value of β fixed in both ZrO_2 and HfO_2 structures to be the same at $\beta = 99.25°$.[17] Earlier during calculations of ZrO_2 we noted that optimization of the Wykoff parameters was needed to explain the relatively low value of the bulk modulus for the ZrO_2 baddeleyite structure. In HfO_2, therefore, we took great lengths to optimize the structure in this way. However the HfO_2 structure proved far less sensitive to Wykoff relaxation when compared with ZrO_2, and this in turn is reflected in the larger value of the bulk modulus for the baddeleyite phase. The calculated properties of the most important phases as obtained through a fit to the Birch equation of state,[20] together with their relative energies, are shown in Table I and the calculated unit-cell parameters of the structures in Table II. Although the reasons for differences between the ZrO_2 and HfO_2 baddeleyite phases are not clear—but likely relate to the extent of electron correlation at higher volume—it can be seen the bulk modulus has increased significantly form the lower coordination baddeleyite structure to the high coordination cotunnite structure in both materials.

Experimental measurements on both ZrO_2 and HfO_2 have revealed that the ambient monoclinic baddeleyite phase of both dioxides transforms under pressure to a series of orthorhombic phases. In the case of ZrO_2, the first orthorhombic phase starts at an applied pressure of about 3 GPa depending upon the grain size of the material and is observed to exist up to about 22 GPa when another orthorhombic structure sets in. The first orthorhombic phase is now identified as having its own orthorhombic-I structure-type with $Pbca$ symmetry[21] and the second a cotunnite structure with $Pnma$ symmetry. On the other hand, for HfO_2 the transformation to the first orthorhombic phase from baddeleyite now sets in at about 4–10 GPa and under pressure the second orthorhombic structure is observed at about 28 GPa and which exists up to about 40 GPa.[14] The structure of quenched samples of the first orthorhombic phase prepared under high-pressure, high-temperature conditions is of the orthorhombic-I $Pbca$-type;[22] however, other structures, $Pbcm$ for example, have been suggested[23] based on *in situ*, high-pressure x-ray diffraction studies. It can be noted that these two space groups along with $Pbc21$, which has been proposed for magnesia partially stabilized zirconia,[24] cannot be distinguished by x-ray diffraction in the case of HfO_2 and in consequence no *in situ* structure refinements have been per-

TABLE II. Calculated crystal structures of some important phases of ZrO_2 and HfO_2. Lattice constants in Å.

Phase	ZrO_2	HfO_2
Baddeleyite ($P2_1/c$)	$a = 5.17$ Zr(0.276,0.41,0.208)	$a = 5.12$ Hf(0.279, 0.042, 0.211)
	$b = 5.23$ O(0.070,0.336,0.341)	$b = 5.17$ O(0.072,0.340,0.343)
	$c = 5.34$ O(0.442,0.755,0.479)	$c = 5.29$ O(0.449,0.758,0.481)
Cotunnite ($Pnma$)	$a = 5.71$ Zr(0.251,0.250,0.109)	$a = 5.48$ Hf(0.249,0.250,0.115)
	$b = 3.25$ O(0.364,0.250,0.422)	$b = 3.35$ O(0.360,0.250,0.425)
	$c = 6.34$ O(0.021,0.750,0.328)	$c = 6.68$ O(0.022,0.750,0.339)
Fluorite ($Fm3m$)	$a = 5.13$ Zr(0.000,0.000,0.000)	$a = 5.14$ Hf(0.000,0.000,0.000)
	O(0.250,0.250,0.250)	O(0.250,0.250,0.250)
Cubic ($Pa3$)	$a = 5.07$ Zr(0.000,0.000,0.000)	$a = 5.26$ Hf(0.000,0.000,0.000)
	O(0.336,0.336,0.336)	O(0.343,0.343,0.343)
Orthorhombic-I ($Pbca$)	$a = 9.94$ Zr(0.885,0.035,0.253)	$a = 10.22$ Hf(0.884,0.033,0.255)
	$b = 5.17$ O(0.799,0.372,0.146)	$b = 5.31$ O(0.791,0.371,0.131)
	$c = 4.94$ O(0.975,0.739,0.496)	$c = 5.08$ O(0.977,0.747,0.494)
$Pbc21$	$a = 5.26$ Zr(0.027,0.263,0.750)	$a = 5.30$ Hf(0.031,0.260,0.752)
	$b = 5.07$ O(0.362,0.067,0.890)	$b = 5.11$ O(0.363,0.069,0.895)
	$c = 5.08$ O(0.227,0.537,0.997)	$c = 5.10$ O(0.230,0.536,0.998)

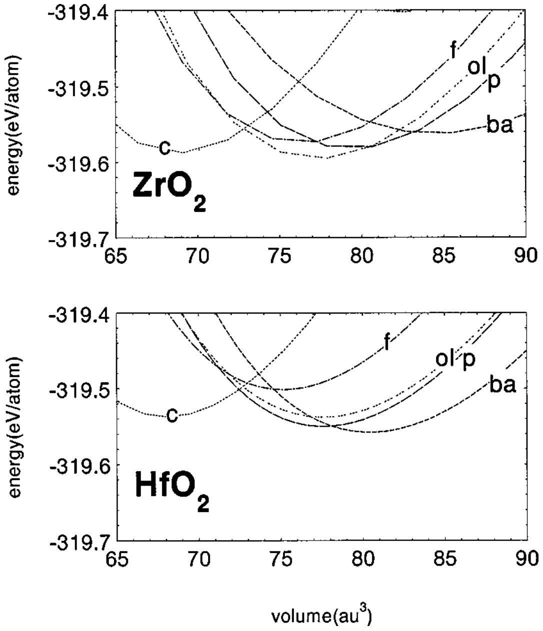

FIG. 2. Calculated energies of ZrO_2 and HfO_2 phases. ba, baddeyelite (Pb_1/c); p, $Pbc21$; oI, orthorhombic-I ($Pbca$); f, fluorite ($Fm3m$); c, cotunnite ($Pnma$).

formed for this phase. The $Pbc21$ structural model can readily be related to that of $Pbcm$. Somewhat simplistically, the 12-atom $Pbc21$ unit cell can nearly twin under a reflection with itself to double up giving the 24-atom $Pbca$ phase.

In Fig. (2) we show the calculated energies of the various phases—energies of the $Pbc21$ and $Pbca$ phases of both oxides lie quite close to each other, but for ZrO_2 the $Pbca$ phase is more stable while for HfO_2 the $Pbc21$ phase is only slightly lower in energy than $Pbca$. In fact, the three phases of HfO_2, $P2_1/c$, $Pbc21$, and $Pbca$, are seen to lie within a very close in energy range (~ 10 meV) of each other. This closeness in energy suggests that the transformation between these phases will be quite sensitive and easily affected by, among other factors, temperature and remnant lattice stresses. It is not, therefore, surprising that there are difficulties in identifying the first orthorhombic phase boundaries of HfO_2 as has been observed experimentally.[15,11,12] A transformation to the second orthorhombic structure is quite clearly also seen for ZrO_2 as involving the structures $Pbca$ into $Pnma$, although again the subtle $Pbc21/Pbca$ interrelation plays a sensitive role in the case of HfO_2. In both ZrO_2 and HfO_2, however, the second orthorhombic phase is clearly $Pnma$, which is in agreement with what is found experimentally.[3,5,11,12] Of course we must bear in mind that our results refer to properties of the pure structures—very often experimental results relate to structures that have been stabilized with other chemicals such as magnesia or yttrium, although the intrinsic approximations in the present computational approach—namely, the use of LDA and our underlying choice of pseudopotentials—clearly must be borne in mind. The important point is that the calculated results show that various phases all lie quite close in energy. The calculated bulk moduli for the harder cotunnite phases, 305 GPa and 306 GPa, respectively, are also in good agreement with the experimental values of 332 GPa for ZrO2 and 340 GPa for HfO2.[5,11] Both theory and experiment thus concur that these phases are highly incompressible.

In summary we have seen through total-energy calculations that there is a general similarity between phases of ZrO_2 and HfO_2, yet the relative ordering in energy of the phases between the two materials has bearing on the formation of the phases, especially the first orthorhombic phase and its formation from the monoclinic baddeleyite phase. The calculated values of the bulk moduli of the high-pressure, cotunnite-type phase agree with experimental results and confirm the low compressibility of these phases. These phases are thus good candidates for hard materials.

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