New Low-Energy Crystal Structures in ZrO₂ and HfO₂

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From first principles, the energy and volume of metastable phases of ZrO₂ and HfO₂ are calculated. At low energy, two inequivalent, nonpolar, orthorhombic phases of the same space group Pbca number P61 are found.

1. Introduction

The simple, binary oxides ZrO₂ and HfO₂ are surprising because of their rich polymorphism and the difficulty of characterization. In earlier years, several new polar and nonpolar phases have been identified, notably the polar orthorhombic phase with space group Pca₂₁ (number P29) with a tremendous potential for ferroelectric applications. The polar P29 was discriminated against nonpolar orthorhombic phase Pcca (number P61) with neutron scattering[1,2] and rediscovered 2011 because of its ferroelectric properties.[3] P61 was found in high-pressure ceramic processing and is therefore labeled high-pressure phase or ortho-I. But it was difficult to discriminate P61 against other orthorhombic phases as Pbcn or Pbcm, which were proposed from a crystallographic point of view.[4] Recently,[5] the P61 was interpreted, based on ab initio calculations, as the horizontal alignment of oppositely polarized P29 conventional cells with the potential for ultimately dense ferroelectric storage. Experimentally, Y-doped HfO₂ in phase P61 could be stabilized under ambient pressure.[6]

Similar to the experimental difficulties, it is not easy to find all the low-energy crystal structures theoretically. With more or less systematic search, with time new crystal phases have been proposed based on ab initio calculations. A polar orthorhombic phase with space group Pmn₂₁ (number P31) was proposed by Huan[7] for HfO₂, but was not found so far experimentally. A variety of new metastable phases were found with a search algorithm from Barabash,[8] but the investigation was limited to 12-atomic cells. Therefore, surprises in the theoretical or experimental efforts can be expected.

In this article, we predict with ab initio calculations a further nonpolar, orthorhombic phase with the second-lowest energy behind the monoclinic P2₁/c (number P14).

2. Computational Methods

The electronic structure calculations were conducted with the all-electron code FHI-AIMS[9] (FHI = Fritz-Haber Institute) using the Perdew–Burke–Ernzerhof solid (PBEsol)[10] density functional, known for good structural results.[11] The calculations were repeated with local-density approximation (LDA) and Perdew–Burke–Ernzerhof (PBE)[12] density functionals and with ABINIT[13] using PBEsol with norm conserving pseudopotentials and LDA with projector-augmented wave (PAW) data sets from the Garrity–Bennett–Rabe–Vanderbilt (GBRV) library.[14] 6 × 6 × 6 and 3 × 6 × 6 k-point grids were used, respectively, for 12- and 24-atomic supercells. With FHI-AIMS, the relaxation was done with Broyden–Fletcher–Goldfarb–Shanno (BFGS) without any constraint on symmetry or lattice constant. With ABINIT the relaxation was done with BFGS with symmetry constraint on space group Pbca (number P61) but without constraint on lattice constant. The convergence criterion for ions was set to 1 × 10⁻³ eV Å⁻¹. The structures were confirmed with the pymatgen[15] library and the Bilbao Crystallographic Server.[16] The dynamical stability of the structures was checked with a phonon calculation at the Γ point. The averaged ionic contribution to the dielectric constant is shown in Table 2.

3. Results and Discussion

For the density functional theory (DFT) calculation, a copy of the 12-atomic conventional cell of Pca₂₁ was reflected at the c-plane, a second copy was additionally reflected at the b-plane and combined. Figure 1 shows the result after relaxation. The first combination yields an antipolar 24-atomic cell of the space group Pcca with oppositely displaced polarizing oxygen, separated by nearly centered spacer oxygen atoms between the polarized regions. This structure features an extremely thin 180° polar domain interface. Instead of periodic boundary condition, polar P29 regions can be attached to the left and right as discussed in the study by Lee et al.[17] The second combination yields space group Pbca (number P61).

The second combination yields after relaxation vertically misaligned metal atoms, an annihilation of the polarization in a layer around the glide plane, sandwiched between spacer layers. Although this structure is nonpolar in itself, polar P29 regions could also be extended to the left and right, leaving still a...
This is surprising. In contrast, a crystal... of HfO$_2$. To distinguish both crystal structures, we name the antipolar... as aP61. Both structures... Table 1, the inequivalent atomic positions are shown in Figure 1, the inequivalent atomic positions are shown in Figure 1. The cif-files are available as Supporting Information.

Both structures have been independently investigated with ab initio calculations, aP61$^{[5,6]}$ and uP61$^{[12]}$ but they have not been compared so far as the coexistence of these structures has not become aware. Compared with the monoclinic phase, the ZrO$_2$ (HfO$_2$) aP61 structure has an energy of only 41.7 meV f.u.$^{-1}$ (44.0 meV f.u.$^{-1}$). But the uP61 structure has even lower energy of only 25.3 meV f.u.$^{-1}$ (28.0 meV f.u.$^{-1}$) and is therefore the lowest energy structure in addition to the monoclinic ground state. The crystal volumes are significantly different. The ZrO$_2$ (HfO$_2$) aP61 structure has a crystal volume of only 267.2Å$^3$/12at (262.3Å$^3$/12at), slightly smaller than the P29 volume. This is consistent with the stabilization at high pressures. The ZrO$_2$ (HfO$_2$) uP61 structure has a crystal volume of only 279.3Å$^3$/12at (274.3Å$^3$/12at), and is even larger than the P14 volume. Stabilization of this phase should be favored under thin-film processing conditions, as different thermal expansion coefficients of film and substrate lead to tensile stress.$^{[11]}$ To show consistency of the calculation, we have included the results for the crystal energy obtained from different methods in Table 2. All methods show the same order of crystal phases according to energy, with the typical differences of LDA predicting lower energy differences than GGA and PBEsol in between. Comparing the neutron diffraction results from Ohtaka for ZrO$_2$$^{[1,2]}$ and HfO$_2$ for position and lattice constant with the calculated values in Table 1, we can clearly identify these as aP61.

The difficulty of identifying the crystal structures in zirconia and hafnia originates in the similarity of metal position, although the nearly invisible oxygen position may be significantly different. We generated an X-ray diffraction (XRD) pattern from the crystal structures with VESTA.$^{[19]}$ Figure 2 shows the comparison of the reflection peaks in the relevant 2θ region 24°–36°. The aP61 is indistinguishable from P29 in the XRD, the uP61 can well be distinguished. If the aP61 has been prepared in thin films, it would appear as the ferroelectric phase portion without polarization under compressive stress. The phases uP61 and aP61 could play a role in the fabrication of ferroelectric HZO films. HZO films have never shown a remanent polarization above 0.2 C m$^{-2}$. The phases uP61 and aP61 are energetically more favorable than P29 and could be present as an unpolarized fraction of the phase mixture of polycrystalline films.

Table 1. Lattice constants, Wyckoff positions, and reduced coordinates of inequivalent atoms of the uP61 and aP61 structures for ZrO$_2$ and HfO$_2$. The energy relative to P14 and the energy of P29 for comparison, calculated with PBEsol (see also Table 2).

|     | ZrO$_2$ | $\Delta E$ | ZrO$_2$ | $\Delta E$ | HfO$_2$ | $\Delta E$ |
|-----|---------|------------|---------|------------|---------|------------|
| uP61| a,b,c [Å] | 5.1869 | 5.2952 | 10.1675 | a,b,c [Å] | 5.1531 | 5.2695 | 10.1028 |
| Zr1 8c | 0.95748  | 0.15732  | 0.36149  | Hf1 8c | 0.95785  | 0.15694  | 0.36153  |
| O1 8c | 0.24842  | 0.41028  | 0.27542  | O1 8c | 0.24749  | 0.41062  | 0.27632  |
| O2 8c | 0.17049  | 0.33423  | 0.03231  | O2 8c | 0.16922  | 0.33315  | 0.03309  |
| aP61| a,b,c [Å] | 5.0709 | 10.0429 | 5.2155 | a,b,c [Å] | 5.0406 | 9.9844 | 5.2155 |
| Zr1 8c | 0.25252  | 0.88466  | 0.46511  | Hf1 8c | 0.25417  | 0.38469  | 0.46437  |
| O1 8c | 0.24842  | 0.79007  | 0.12305  | O1 8c | 0.12775  | 0.29038  | 0.12486  |
| O2 8c | 0.99769  | 0.97748  | 0.73880  | O2 8c | 0.99742  | 0.02322  | 0.23872  |
| P29| a,b,c [Å] | 5.0406 | 9.9844 | 5.2155 | a,b,c [Å] | 5.0406 | 9.9844 | 5.2155 |

Figure 1. a) Antipolar Pbca structure aP61, and b) nonpolar Pbca structure uP61. The arrows indicate the oxygen atoms responsible for polarization.
To complete the survey of low-energetic crystal structures, we have calculated the energy and volume of some other low energy phases. P31 is a polar orthorhombic phase. P215 is a cubic phase which is significantly lower in energy than the usually discussed high symmetry phase P225. Table 2 collects the data for energy and volume.

### Table 2. Calculated volume of crystal structures per 12 atomic cell. Experimental volumes from collection in the study by Falkowski and Kersch\textsuperscript{[18]} are in brackets. Calculated energies of crystal structures relative to the monoclinic phase, calculated with different methods. Averaged ionic contribution to the dielectric constant $\varepsilon_{\text{ave}}$.

| ZrO$_2$ | Space group | Volume [Å$^3$/12at] | Energy [meV f.u.$^{-1}$] | $\varepsilon_{\text{ave}}$ Ionic |
|---------|-------------|------------------|--------------------------|-----------------|
| P14     | $P_{21/c}$  | 278.9 (281.9)    | 0                        | 0               |
| uP61    | $P_bca$     | 279.3            | 25.3                     | 26.6            |
| aP61    | $P_bca$     | 267.2 (270.2)    | 41.7                     | 67.9            |
| P29     | $P_{cc2}$   | 269.0 (270.7)    | 52.9                     | 72.3            |
| P137    | $P_{4/n}nc$ | 265.8 (268.1)    | 78.3                     | 109.8           |
| P31     | $P_{mmn}$   | 269.5            | 94.2                     | –               |
| P215    | $P_{43m}$   | 273.1            | 99.4                     | –               |
| P225    | $Fm\bar{3}m$ | 259.6          | 145.2                    | –               |

| HfO$_2$ | Space group | Volume [Å$^3$/12at] | Energy [meV f.u.$^{-1}$] | $\varepsilon_{\text{ave}}$ Ionic |
|---------|-------------|------------------|--------------------------|-----------------|
| P14     | $P_{21/c}$  | 273.9 (276.3)    | 0                        | 0               |
| uP61    | $P_{bca}$   | 274.3            | 28.0                     | 33.7            |
| aP61    | $P_{bca}$   | 262.3 (264.9)    | 44.0                     | 52.3            |
| P29     | $P_{cc2}$   | 264.2 (268.9)    | 60.5                     | 78.0            |
| P137    | $P_{4/n}nc$ | 262.5 (266.4)    | 134.8                    | 134.5           |
| P31     | $P_{mmn}$   | 262.5            | 133.8                    | –               |
| P215    | $P_{43m}$   | 259.9            | 158.5                    | –               |
| P225    | $Fm\bar{3}m$ | 256.4          | 214.1                    | –               |

\textsuperscript{a}FHI-AIMS with tier 2 basis set; \textsuperscript{b}ABINIT with PAW from GBRV library.

Figure 2. a, b) Simulated XRD patterns of the calculated crystal structures: a) P137, P29, aP61, uP61, P14, and b) P31, P29, P215, P225, P14 of ZrO$_2$ at a wavelength of 1.54059 Å.

To complete the survey of low-energetic crystal structures, we have calculated the energy and volume of some other low energy phases. P31 is a polar orthorhombic phase. P215 is a cubic phase which is significantly lower in energy than the usually discussed high symmetry phase P225. Table 2 collects the data for energy and volume.

### 4. Conclusion

We report the observation of two low-energy crystal structures of the same space group of number P61, which are inequivalent. This is surprising, but the space group does not determine the structure uniquely. The structures can be distinguished by...
considering them as two possible horizontal arrangements of oppositely polarized P2\(_1\) polar phase structures, but with antipolar (aP6\(_1\)) and nonpolar (uP6\(_1\)) compensation of the respective polarizations. The relaxed energies of the structures are very low, and they constitute the lowest energetic structures above the monoclinic ground state. The crystal volumes are significantly different. We expect that both crystal structures play a role in the polymorphism of ZrO\(_2\) and HfO\(_2\) and the related ferroelectricities.

Note added after online publication: After initial Early View publication, the authors were informed of work by Du et al.\(^{[20]}\) that was published shortly before submission of this paper, of which they were previously unaware, and which contains an experimental observation of the nonpolar Pbca crystal phase. The antipolar Pbca has already been observed experimentally 1990 by Ohtaka et al.\(^{[1]}\) The work by Du et al.\(^{[20]}\) also contains also a theoretical comparison of the antipolar Pbca and the nonpolar Pbca, the latter being first published in 2015 by Materlik et al.\(^{[17]}\)

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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antiferroelectricity, ZrO\(_2\), HfO\(_2\), ferroelectricity, structure predictions

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