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First-principles investigation of Zr-O compounds, their crystal structures, and mechanical properties

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First-principles evolutionary simulations are used to systematically predict stable compounds in the Zr-O system at pressures up to 120 GPa. Zr-O compounds and Hf-O compounds share many similarities, but four new phases Cmmm-Zr3O, R3c-ZrO2, Pnma-ZrO, and Fe2P-type ZrO2 (P62m) appear in the Zr-O system: the latter two phases appear in the Hf-O system at higher pressure. OIi-ZrO2 (Pnma) transforms into Fe2P-type ZrO2 at 102 GPa. Meanwhile, Fe2P-type ZrO2 and P62m-ZrO have similar structures based on ω-Zr. However, the calculated Vickers hardness of Fe2P-type ZrO2 (5.6 GPa) is inferior to that of P62m-ZrO (14.1 GPa). The hardness of P62m-ZrO (14.1 GPa) is lower than that of P62m-HfO (16.1 GPa) and P62m-TiO (16.6 GPa). On the whole, Zr-O compounds exhibit lower hardnesses and bulk moduli than Hf-O compounds. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4979913]

INTRODUCTION

Zirconia (ZrO2) is an important and attractive ceramic oxide with good mechanical properties, high melting point, and remarkable chemical inertness. Pressure-induced phase transitions of ZrO2 had been experimentally and theoretically investigated. Experiments indicated that baddeleyite (P21/c-ZrO2) transforms into orthorhombic-I (Pbaa-ZrO2, OI) at 3–4 GPa (Ref. 1) (10 GPa (Ref. 2)), then into cotunnite (Pnma-ZrO2, OII) phase at 12.5 GPa (Ref. 1) (25 GPa (Ref. 2)). Cotunnite ZrO2 was believed to be stable up to at least 100 GPa, and the recent high-pressure laser-heated diamond-anvil cell (LH-DAC) experiment11 reported that cotunnite ZrO2 transformed into a post-cotunnite ZrO2 (Fe2P-type) at 175 GPa and 3000 K.

Besides ZrO2, zirconium-rich zirconium Zr2O3 was experimentally reported in Morant’s3 and Nishino’s work4 without providing its crystal structure. Recently, semimetallic P4/min-Zr2O3 was theoretically predicted by Xue.5 In addition, Furuta and Motohashi6 found a cubic ZrO (a = 4.62 Å) on a zirconoy oxidized in steam at 1000 °C. Ni7 observed thin intermediate oxide layers with composition close to ZrO. Theoretical calculations8–10 indicated that hexagonal P62m-ZrO instead of NaCl-type ZrO is the ground state of zirconium monoxide, and P62m-ZrO should be stable up to 100 K.8,9 Even though P62m-ZrO had not been experimentally reported, just recently, the experiment11 successfully synthesized the P62m-TiO by using a bismuth flux and demonstrated that NaCl-type TiO was actually a high-temperature phase.

Other stoichiometries of zirconium suboxides can be formed in a thin suboxide layer at the metal/oxide interface during oxidation of zirconium alloys. According to previous experimental reports on oxygen-intercalated α-Zr, compounds with O/Zr ≤ 1/3 designated as ZrO belong to R3c space group,12,13 while compounds with O/Zr ≥ 1/3 designated as ZrOx belong to P62m space group.14 At the same time, Zr6O suboxide was detected in thin foils of oxidized zirconium by selected area diffraction15 and then Arai16 reported the structure of Zr6O to be isomorphic with P31c-Ti6O. In addition, ε-Fe2N type Zr2O was proposed using X-ray and neutron diffraction in Hashimoto’s work.17 First-principles calculations8,9,18 indicated that R3-Zr6O, R3c-Zr5O and P31m-Zr2O were ground-state structures.

Zirconium and hafnium belong to the same group in the Periodic Table. Because of lanthanide contraction, the ionic radius of hafnium (Hf4+) is slightly smaller (by 0.01 Å) than that of zirconium (Zr4+)19, and chemical properties of Hf and Zr are very similar. Due to their identical chemistry, Hf concentrates in all of the zirconium ores (mainly zircon and baddeleyite) and it is difficult to separate these two elements. However, hafnium possesses a closed f-electron subshell ([Kr]4d55s2), while zirconium has no f-electrons ([Xe]4f145d26s2), another noticeable difference is that neutron
absorption cross-section of hafnium is 600 times higher than that of zirconium. In our previous work, the Hf-O system at pressures up to 120 GPa was studied by first-principles calculations, while a comparative investigation of the Zr-O system is presented here.

**COMPUTATIONAL METHODOLOGY**

Stable compounds and structures in the Zr-O system are searched at pressure up to 120 GPa by using the first-principles evolutionary algorithm (EA) as implemented in the USPEX code combined with *ab initio* structure relaxations using density functional theory (DFT) with the PBE-GGA (Perdew-Burke-Ernzerhof Gradient Generalized Approximation) functional, as implemented in the VASP (Vienna Ab initio Simulation Package) package. The electron-ion interaction was described by scalar relativistic projector-augmented wave (PAW) potentials, with 4s2 4p6 5s2 4d2 and 2s2 2p4 shells treated as valence for Zr and O, respectively. Variable-composition structure searches were performed at 0 GPa, 10 GPa, 20 GPa, 30 GPa, 40 GPa, 50 GPa, 60 GPa, 70 GPa, 80 GPa, 90 GPa, 100 GPa, 110 GPa, and 120 GPa for the Zr-O system with up to 32 atoms in the primitive unit cell. The first generation of structures were created randomly; then, energetically worst structures were discarded, and a new generation was created from the remaining structures through heredity (40%), lattice mutation (20%), random symmetric generator (20%), and transmutation (20%). After structure searches identified potentially stable phases, we explored pressure-induced structural phase transformation and elastic properties of Zr-O compounds, all results are based on carefully relaxed structures and well-converged plane-wave energy cutoff (600 eV) and Γ-centered uniform k-meshes (2π × 0.06 Å⁻¹). Phonon dispersions were calculated using the finite-displacement method as implemented in the Phonopy code. Voigt-Reuss-Hill (VRH) approximation was adopted to estimate polycrystalline bulk (B) and shear moduli (G).

**RESULTS AND DISCUSSION**

The pressure-composition phase diagram of the Zr-O system is shown in Fig. 1(a). Compared with the phase diagram of the Hf-O system, several new phases including Cmmm-Zr3O, R3c-Zr12O5, Pnma-ZrO, and Fe3P-type ZrO2 appear on the Zr-O phase diagram. Predicted pressure ranges of stability of all the Zr-O phases are listed in Table I. Dynamical stabilities of all the high-pressure phases at 0 GPa were checked by calculating their phonon dispersion curves (see supplementary material, Fig. S1).

![Diagram](image-url)

**FIG. 1.** (a) Pressure-composition phase diagram of the Zr-O system at pressures below 120 GPa. The phase diagram of Hf-O system (reproduced with permission from Phys. Rev. B 92, 184104-3 (2015). Copyright 2015 American Physical Society) below 120 GPa is drawn as a reference. Compounds, which appear in the Zr-O system, but are not stable in the Hf-O system, are highlighted in blue.
stable up to 11.5 GPa. Semimetallic $P\bar{4}m2$-Zr$_2$O$_3$, which was also predicted in Xue’s work, is a metastable phase at zero pressure and becomes stable above 4.4 GPa. $P6\bar{2}m$-ZrO and $P6\bar{2}m$-HfO are formed on $\omega$-Zr and $\omega$-Hf, and exhibit interesting structures and electronic properties. Besides, $P6\bar{2}m$-TiO has been proven to be the ground state of titanium monoxide and it has been experimentally detected using XRD in Amano’s work. There is a phase transition for ZrO at 72 GPa, from the hexagonal $P6\bar{2}m$-ZrO with fivefold coordination of oxygen atoms to an orthorhombic $Pnma$-ZrO structure with sixfold coordination of oxygens (Fig. 5(a)). For curiosity, we calculated the enthalpies of $P6\bar{2}m$-HfO and $Pnma$-HfO as a function of pressure and found that $P6\bar{2}m$-HfO transforms into $Pnma$-HfO at 123 GPa (Fig. 5(b)). The structure of $Pnma$-ZrO is shown in Fig. 4(a).

With increasing pressure, monoclinic baddeleyite ZrO$_2$ transforms into OI-ZrO$_2$ at 7 GPa and then into cotunnite ZrO$_2$ at 11.4 GPa, compatible with previous GGA results (baddeleyite ZrO$_2$ to OI ZrO$_2$ at 6.6 GPa (7.9 GPa); OI ZrO$_2$ to cotunnite ZrO$_2$ at 9.2 GPa (13 GPa)); and experimental results (baddeleyite ZrO$_2$ to OI ZrO$_2$ at 3–4 GPa; OI ZrO$_2$ to cotunnite ZrO$_2$ at 12.5 GPa). Very recently, Nishio-Hamane demonstrated the appearance of the Fe$_2$P-type ZrO$_2$ at 175 GPa and 3000 K and their GGA-calculated transition pressure was 143 GPa. Our calculations indicate, as shown in Fig. 5(c), that cotunnite ZrO$_2$ transforms into Fe$_2$P-type ZrO$_2$ at 102 GPa, which is lower than the above mentioned experimental and calculated transitional pressures. This is an unusually large difference, the origin of which is unclear to us, but our computed phase transition pressure from cotunnite TiO$_2$ to Fe$_2$P-type TiO$_2$ is 151 GPa, in excellent agreement with the previously calculated 149.5 GPa (Ref. 32) and 147 GPa (Ref. 33) in GGA. At the same time, larger values were reported too: 161 GPa and 0 K from DFT-GGA calculation and 210 GPa and 4000 K from experiments of Dekura et al. in laser-heated diamond anvil cells. Fe$_2$P-type HfO$_2$ was not found in the previous high-pressure study of the Hf-O system at pressures below 120 GPa and it has not been experimentally reported. However, Hf resides in the same group as Zr and Ti, and shares many similarities with Zr, so it is natural for us to expect that Fe$_2$P-type HfO$_2$ appears at a certain high pressure. Indeed, according to our calculated enthalpy-pressure diagrams of HfO$_2$ (Fig. 5(d)), Fe$_2$P-type HfO$_2$ occurs at 136 GPa. Lattice parameters, bulk moduli, and their pressure derivatives for $P6\bar{2}m$-ZrO, $P6\bar{2}m$-HfO, $P6\bar{2}m$-TiO, Fe$_2$P-type ZrO$_2$, Fe$_2$P-type HfO$_2$, and Fe$_2$P-type TiO$_2$ are listed in Table II.
On the basis of the above analysis, we can conclude that the high-pressure Fe$_2$P-type TiO$_2$, Fe$_2$P-type ZrO$_2$, and Fe$_2$P-type HfO$_2$ appear at 149.5 GPa, 102 GPa, and 136 GPa, respectively. Fe$_2$P-type HfO$_2$ appears at a higher pressure than Fe$_2$P-type ZrO$_2$. Actually, the transition pressures from baddeleyite HfO$_2$ to OI HfO$_2$ and then to cotunnite HfO$_2$ are also higher than those in ZrO$_2$. Generally, as one goes down the group in the Periodic Table, the atoms get larger and more compressible. As a consequence, lower pressures are required for phase transitions. However, due to lanthanide contraction (which is a relativistic effect), Hf is less compressible and slightly smaller than Zr, reversing the normal trend. The influence of lanthanide contraction can also explain why ZrO$_3$ becomes stable at 80.3 GPa, much lower than 110 GPa for HfO$_3$. Similar to HfO$_3$, ZrO$_3$ contains oxide ion O$^{2-}$ and peroxide ion [O-O]$^{2-}$. At 0 GPa, the O-O distances of [O-O]$^{2-}$ are 1.484 Å in ZrO$_3$ and 1.490 Å in HfO$_3$, which are comparable to those in SrO$_2$ (1.483 Å) and BaO$_2$ (1.493 Å) at normal conditions.\(^{38}\)

As shown in Figs. 6(a)–6(c), structures of $\omega$-Zr, $P6_2m$-ZrO, and Fe$_2$P-type ZrO$_2$ share interesting similarities with HfO$_3$, which are comparable to those in SrO$_2$ (1.483 Å) and BaO$_2$ (1.493 Å) at normal conditions.\(^{38}\)

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each other. \(\omega\)-Zr consists of an alternating Zr-graphene layer (A) and Zr layer (B), so it has ABABAB stacking sequence. The crystal structure of \(P62m\)-ZrO has oxygen atoms occupying the voids in the Zr layer (B) of \(\omega\)-Zr, which is represented as B'. Thus, \(P62m\)-ZrO has an AB'AB'AB' stacking sequence. With increasing pressure, oxygen atoms dissolve into the voids of both the Zr layer (B) and Zr-graphene layer (A) in \(\omega\)-Zr, leading to the Fe\(_2\)P-type structure of ZrO\(_2\). The Zr-graphene layer (A) with O atoms occupying the voids can be denoted as A'; therefore, the layer sequence in Fe\(_2\)P-type ZrO\(_2\) is A'B'AB'B'A'.

\(R3\)-ZrO, \(R3c\)-ZrO, \(Cm\text{m}m\)-Zr\(_3\)O, \(I\text{m}m\text{m}2\)-Zr\(_3\)O\(_2\), \(R3\)-Zr\(_3\)O\(_5\), \(P31m\)-ZrO, \(P\text{m}n\text{m}\)-Zr\(_3\)O\(_2\), \(I41\text{amd}\)-Zr\(_2\)O, and \(R3c\)-Zr\(_3\)O\(_3\) are metallic materials. \(P\bar{6}2m\)-ZrO, \(P\text{m}n\text{m}\)-ZrO\(_2\), and \(P4\text{m}2\)-Zr\(_2\)O\(_3\) are semimetallic. The semimetallic character of \(P\text{m}n\text{m}\)-ZrO comes from the slight overlap of the valence and conduction bands at different symmetry points, as a result, both electron and hole pockets occur in the Fermi surface, see the band structure calculated with the hybrid functional HSE06 in Fig. 4(b). \(P2\(_1\)/c\)-ZrO\(_2\), \(P\text{b}c\text{a}\)-Zr\(_3\)O\(_2\), \(P\text{m}n\text{m}\)-Zr\(_3\)O\(_2\), and \(P\text{m}n\text{m}\)-Zr\(_3\)O\(_3\) are insulators.

The elastic moduli (polycrystalline bulk modulus \(B\), shear modulus \(G\), and Young’s modulus \(E\), Poisson’s ratio \(\nu\), and hardness of all the Zr-O compounds at 0 GPa are summarized in Table III. Zr\(_3\)O has the lowest hardness among Zr-O compounds. According to the Pugh criterion,\(^{36}\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(C_{11})</th>
<th>(C_{12})</th>
<th>(C_{13})</th>
<th>(C_{44})</th>
<th>(G)</th>
<th>(B)</th>
<th>(E)</th>
<th>(\nu)</th>
<th>(H)</th>
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<td>207</td>
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<td>154</td>
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<td>408</td>
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<td>126</td>
<td>142</td>
<td>55</td>
<td>-21</td>
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<tr>
<td>(P2(_1)/c)-Zr(_3)O(_2) (Ref. 36)</td>
<td>337</td>
<td>351</td>
<td>268</td>
<td>79</td>
<td>70</td>
<td>114</td>
<td>155</td>
<td>84</td>
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<tr>
<td>(P\text{b}c\text{a})-Zr(_3)O</td>
<td>332</td>
<td>389</td>
<td>339</td>
<td>86</td>
<td>83</td>
<td>113</td>
<td>151</td>
<td>121</td>
<td>122</td>
</tr>
<tr>
<td>(P\text{b}c\text{a})-Zr(_3)O(_2) (Ref. 36)</td>
<td>349</td>
<td>397</td>
<td>352</td>
<td>87</td>
<td>84</td>
<td>115</td>
<td>150</td>
<td>125</td>
<td>120</td>
</tr>
<tr>
<td>(P\text{m}n\text{m})-Zr(_3)O (_2)</td>
<td>413</td>
<td>296</td>
<td>334</td>
<td>49</td>
<td>74</td>
<td>115</td>
<td>146</td>
<td>177</td>
<td>120</td>
</tr>
<tr>
<td>(P\text{m}n\text{m})-Zr(_3)O (_2) (Ref. 36)</td>
<td>422</td>
<td>293</td>
<td>327</td>
<td>52</td>
<td>70</td>
<td>117</td>
<td>145</td>
<td>178</td>
<td>114</td>
</tr>
<tr>
<td>(P62m)-Zr(_3)O</td>
<td>383</td>
<td>386</td>
<td>116</td>
<td>266</td>
<td>150</td>
<td></td>
<td>252</td>
<td>91</td>
<td>245</td>
</tr>
<tr>
<td>(P\text{m}n\text{m})-Zr(_3)O</td>
<td>338</td>
<td>265</td>
<td>317</td>
<td>47</td>
<td>58</td>
<td>125</td>
<td>134</td>
<td>86</td>
<td>79</td>
</tr>
</tbody>
</table>

FIG. 6. Crystal structures and (001) sections of the electron localization function (ELF) for hcp-Zr in (a) and (d), \(P62m\)-ZrO in (b) and (e) and \(P62m\)-Zr\(_3\)O in (c) and (f). Red spheres–O atoms; green spheres–Zr atoms.
$G/B > 0.57$ characteristic of a brittle material and $G/B < 0.57$ corresponds to a ductile material. Thus, the most brittle Zr-O compounds include $I mm 2-ZrO_2$, $P mm 2-ZrO_2$, and $P 62 m-ZrO_2$, while $P 62 m-ZrO_2$ with $G/B = 0.36$ is surprisingly the most ductile.

$P 62 m-ZrO_2$ is the hardest among Zr-O compounds, and the calculated hardness of $P 62 m-ZrO_2$ is 14.1 GPa, which is lower than that of $P 62 m$-HfO (16.1 GPa) and of $P 62 m$-TiO (16.6 GPa). Interestingly, $P 62 m-ZrO_2$, which shares strong structural similarities with $P 62 m-ZrO$, exhibits a low hardness (5.6 GPa). The only structural difference between these two phases is that $P 62 m-ZrO$ has pure Zr-graphene layers (A) and $P 62 m-ZrO_2$ has oxygen present in these Zr-graphene layers (A'). We therefore can infer that the oxygen dissolved in Zr-graphene layers has a negative effect on the hardness of $P 62 m-ZrO_2$. In order to understand this phenomenon, electron localization function (ELF) of $P 62 m-ZrO$ and $P 62 m-ZrO_2$ was calculated and analyzed, see Figs. 6(e) and 6(f). There are high electron concentrations (red areas in Fig. 6(e)) in the center of the hexagonal Zr ring, indicating multicenter covalent bonding within A layer of $P 62 m-ZrO$. As oxygen atoms enter this layer, this multicenter covalent bonding disappears, giving way to ionic Zr-O bonds and a decrease of the hardness.

**CONCLUSIONS**

In summary, we have predicted the pressure-composition phase diagram of the Zr-O system. The most striking differences between Zr-O and Hf-O systems are: (1) lower transition pressures in the Zr-O system (contrary to the usual trend, and due to the relativistic “lanthanide contraction” affecting the Hf atom), and (2) lower elastic properties and hardnesses of Zr-O compounds. Interestingly, $P 62 m-ZrO_2$ and Fe$_2$P-type Zr$_2$O$_4$ are both based on $\omega$-Zr, but the calculated Vickers hardness of Fe$_2$P-type Zr$_2$O$_4$ (5.6 GPa) is much lower than that of $P 62 m-ZrO$ (14.1 GPa) due to more ionic bonds in $P 62 m-ZrO_2$ than in $P 62 m$-Zr-O compounds. The hardness of $P 62 m-ZrO_2$, which is the highest among Zr-O compounds, is smaller than that of $P 62 m$-HfO (16.1 GPa) and $P 62 m$-TiO (16.6 GPa).

**SUPPLEMENTARY MATERIALS**

See supplementary material for calculated structural parameters and calculated phonon dispersion curves of Zr-O compounds at 0 GPa.

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