The prediction of a new high-pressure phase of hafnia using first-principles computations

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Abstract. Using density functional theory (DFT) calculations, we predicted a new high-pressure phase of hafnia (HfO2). We found the hexagonal phase (Ni2In-type structure; space group: P63/mmc) to be the stable phase at ultrahigh pressures greater than ~386 GPa. Our findings are consistent with recent calculations performed on the similar dioxide ZrO2 [M. Durandurdu, J. Solid State Chem. 230, 233 (2015)] where this phase has been claimed to be the most stable at pressures greater than 380 GPa. The Birch-Murnaghan equation of state (BM-EOS) of the new phase shows that this phase is more compressible and less dense than Fe2P-type phase. Additionally, the hardness calculations using a scaling model confirmed that our newly predicted phase has a similar hardness compared to the other HfO2 phases, indicating that none of the HfO2 phases can be considered to be superhard.

1. Introduction

Hafnia (HfO2) is an important dioxide that has been involved in many industrial and technological applications. It has important optical properties [1–4], and it is also considered as a good candidate to replace silicon dioxide (SiO2) in electronic devices due to its high dielectric constant and thermal stability [5–8]. Additionally, the structural and mechanical properties of HfO2 have received an extensive attention, where the high-pressure/temperature behavior of HfO2 is considered as one of the important research directions in studying this dioxide both experimentally [9–18] and theoretically [9], [19–23].

Experimental observations [9, 11, 24] and first-principles computations [9, 20, 23] agree that the well-known high-pressure phase transition sequence for HfO2 is as follows: MI (Baddeleyite) \( \rightarrow \) OI (Orthorhombic I) \( \rightarrow \) OII (Orthorhombic II or cotunnite). However, recently, a theoretical and experimental evidence for a new high-pressure post-OII phase (called Fe2P phase) (Fig. 1) for HfO2 has been claimed [25], in good agreement with the recently reported results in the similar dioxides ZrO2 [26] and TiO2 [27]. Experimentally, Fe2P phase is found to be stable at extreme pressure-temperature (P-T) conditions that exceeds (175 GPa, 3000 K) for ZrO2 [26], (210 GPa, 4000 K) for TiO2 [27], and (105 GPa, 2000 K) for HfO2 [25]. On the other hand, the theoretical stability of Fe2P phase is predicted to be at pressures greater than 143 GPa (for ZrO2) [26], 161 GPa (for TiO2) [27], and 120-140 GPa (for HfO2) [25]. Consequently, the updated experimental and theoretical high-pressure phase transition sequence in these three dioxides becomes as follows: MI \( \rightarrow \) OI \( \rightarrow \) OII \( \rightarrow \) Fe2P.
Recently, a new phase (called Ni\textsubscript{2}In) (Fig. 1) has been theoretically tested for ZrO\textsubscript{2} [28], and it has been predicted to be stable at very high pressures greater than 380 GPa. In fact, it should be noted that the transition to Ni\textsubscript{2}In phase has been claimed to occur directly from OII phase and not from Fe\textsubscript{2}P phase, which is not consistent with the recent calculations and measurements performed on HfO\textsubscript{2} [25], ZrO\textsubscript{2} [26] and TiO\textsubscript{2} [27]. This finding proves that Fe\textsubscript{2}P-type phase is a post-OII phase. However, we should also note that the enthalpy differences between OII and Fe\textsubscript{2}P phases are very small [25–28], and, therefore, comparable transition pressures across OII \rightarrow Ni\textsubscript{2}In versus Fe\textsubscript{2}P \rightarrow Ni\textsubscript{2}In are likely.

To the best of our knowledge, the high-pressure phase stability of Ni\textsubscript{2}In has not been previously tested for HfO\textsubscript{2}. In this study, we use DFT calculations to test the stability and investigate the EOS of Ni\textsubscript{2}In phase at high pressures for HfO\textsubscript{2} in order to better understand the phase diagram of this important dioxide.

### 2. Computational Method

DFT calculations are used to investigate the phase transformation and the EOSs of HfO\textsubscript{2} [29]. The projector-augmented wave (PAW) formalism [30, 31] was used to treat the interactions between the atoms having a core radii of 2.600 Bohr for hafnium Hf (with the valence configuration of 5\textit{p}\textsuperscript{6}6\textit{s}\textsuperscript{2}5\textit{d}\textsuperscript{2}) and 1.520 Bohr for oxygen O (with the valence configuration of 2\textit{s}\textsuperscript{2}2\textit{p}\textsuperscript{4}). The generalized gradient approximation (GGA) [32] was used to treat the electronic exchange and correlation effects. We performed our calculations using VASP software package [33–36] with an energy cutoff of 600 eV and \Gamma-centered \textit{k}-point meshes [37]. For both phases, total energies and pressures were converged to better than \textasciitilde 0.1 meV/atom and \textasciitilde 0.1 GPa, respectively. The Brillouin zone integration was performed using the following \textit{k}-point meshes for the HfO\textsubscript{2} phases: 6x6x10 for Fe\textsubscript{2}P and 10x10x8 for Ni\textsubscript{2}In. For a fixed volume, all internal degrees of freedom and unit-cell parameters of the structure were optimized simultaneously during the geometry optimizations. The ground-state energy for each phase was determined for 13–16 volumes. Up to highest pressure achieved in our calculations, both HfO\textsubscript{2} phases remain insulators.
3. Results and Discussion
3.1. Birch-Murnaghan equation of state determination
The applied pressure \( P \) in the third-order BM-EOS [38] is expressed as follows:

\[
P(V) = \frac{3}{2} K_0 \left[ \left( \frac{V}{V_0} \right)^{7/3} - \left( \frac{V}{V_0} \right)^{5/3} \right] + \frac{3}{4} K_0' \left( \frac{V}{V_0} \right)^{5/3} - 1 \right] + E_0
\]

Eqn. (1)

where \( V \) is the volume at pressure \( P \), \( V_0 \) is the zero-pressure volume, \( K_0 \) is the zero-pressure Bulk modulus, and \( K_0' \) is the first pressure derivative of the bulk modulus at zero pressure. From the following thermodynamic relationship: \( P(V) = -\frac{\partial E}{\partial V} \), one can obtain an expression for the total energy \( E \) in the third-order form of BM-EOS as follows:

\[
E(V) = \frac{9}{2} K_0 V_0 \left\{ \frac{1}{2} \left( \frac{V}{V_0} \right)^{5/3} - 1 \right\} \left[ \left( \frac{V}{V_0} \right)^{7/3} - \left( \frac{V}{V_0} \right)^{5/3} \right] + E_0
\]

Eqn. (2)

where \( E_0 \) is the total energy at zero pressure. The second-order BM-EOS is obtained by fixing \( K_0' \) to 4 in Eqns. 1 and 2 to get the following second-order expressions:

\[
P(V) = \frac{3}{2} K_0 \left[ \left( \frac{V}{V_0} \right)^{7/3} - \left( \frac{V}{V_0} \right)^{5/3} \right] + E_0
\]

Eqn. (3)

\[
E(V) = \frac{9}{4} K_0 V_0 \left( \frac{V}{V_0} \right)^{7/3} - 1 \right\} + E_0
\]

Eqn. (4)

The EOS parameters for each phase were obtained by fitting the total energy as a function of volume (Eqns. 2 and 4) to a second- and a third-order BM-EOS [38] (Table I).

The calculated EOS parameters for Fe\(_2\)P and Ni\(_2\)In phases of HfO\(_2\) are summarized in Table I. For comparison, we listed values from recent work on Fe\(_2\)P-HfO\(_2\) [25], which are in excellent agreement with our calculations. To the best of our knowledge, the Ni\(_2\)In phase has not been previously tested for the HfO\(_2\) case, but it has been tested for the similar dioxide ZrO\(_2\) [28]. Table I shows that our calculated EOS parameters for Ni\(_2\)In-HfO\(_2\) agree well with its analog Ni\(_2\)In-ZrO\(_2\).

Futhermore, one can see an appreciable decrease in the bulk modulus upon the transformation from Fe\(_2\)P to Ni\(_2\)In phase. The calculated second-order BM-EOS shows that the Bulk modulus decreases by ~24%, indicating that Ni\(_2\)In is much more compressible than Fe\(_2\)P. However, this decrease is not unexpected as this transformation between the two phases is associated with an increase in the zero-pressure volume \( V_0 \) of ~2.6% and an increase in the coordination number (CN) from 9 (for Fe\(_2\)P) to 11 (for Ni\(_2\)In). We should mention that the increase in the CN is not necessarily associated with \( V_0 \) increase (and thus \( K_0 \) decrease). For instance, for HfO\(_2\) and other similar dioxides ZrO\(_2\) [39] and TiO\(_2\) [40], the transformation from OI phase to OII phase is associated with a CN increase from 7 to 9 and a \( V_0 \) decrease (and thus \( K_0 \) increase).

**Table I:** Theoretical EOSs of Fe\(_2\)P and Ni\(_2\)In phases of HfO\(_2\). For comparison, we list other theoretical results for HfO\(_2\) [25] and ZrO\(_2\) [28]. 1σ uncertainties are given in parentheses.

| Phase | \( V_0 (\text{Å}^3) \) | \( K_0 \) (GPa) | \( K_0' \) | Reference |
|-------|----------------|----------------|------------|-----------|
| Fe\(_2\)P | 29.69 (0.03) | 288 (2) | 4 (fixed) | Ref. [25] |
|       | 29.74 (0.01) | 270 (1) | 4.32 (0.02) | Ref. [25] |
|       | 29.73 (0.02) | 282 (2) | 4 (fixed) | This work |
To better understand the high compressibility of Ni$_2$In phase, we have looked at the variation of the unit-cell parameters with pressure (Fig. 2). Figure 2 clearly shows the dramatic decrease in $c/a$ ratio up to ~50 GPa, after which it continues to decrease with increasing pressure but with a lower rate. We can also conclude that the unit-cell parameter $c$ is much more compressible than the parameter $a$; therefore, the high compressibility in $K_0$ is likely due to the high compressibility along the unit-cell parameter $c$.

|                | 29.74 (0.01) | 268 (1) | 4.39 (0.02) |
|----------------|-------------|---------|-------------|
| Ni$_2$In       | 29.21       | 239     | 3.86        |
|                | 30.49 (0.14)| 213 (6) | 4 (fixed)   |
|                | 31.18 (0.05)| 151 (2) | 5.29 (0.07) |

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3.2. High-pressure phase transition
Our enthalpy calculations for the two phases (Fig. 3) show that the transition pressure from Fe$_2$P to Ni$_2$In occurs at ~387 GPa and 386 GPa using the second- and third-order BM-EOS, respectively. The transition at such ultrahigh pressure is supported by the result recently obtained for the OII $\rightarrow$ Ni$_2$In transition in ZrO$_2$ [28] at 380 GPa, where the enthalpy differences are very small between OII and Fe$_2$P [28] and, thus, the Fe$_2$P $\rightarrow$ Ni$_2$In for ZrO$_2$ should occur at a pressure close to 380 GPa. Therefore, our calculated transition pressure across Fe$_2$P $\rightarrow$ Ni$_2$In in HfO$_2$ is very reasonable when compared to its analog dioxide ZrO$_2$.

![Figure 2: $c/a$ ratio for Ni$_2$In-ZrO$_2$ phase as a function of pressure.](image)
Figure 3: Change in enthalpy with respect to Fe$_2$P phase versus pressure of one HfO$_2$ formula unit.

The transition pressure from Fe$_2$P to Ni$_2$In is $\sim$387 GPa and $\sim$386 GPa using a second- (dashed curve) and third- (solid curve) order BM-EOS [38], respectively.

In our recent theoretical study on HfO$_2$ [25], we found that the OII $\rightarrow$ Fe$_2$P transition occurs at $\sim$120-140 GPa. Consequently, the updated upper high-pressure phase transition sequence for HfO$_2$ is: OII $\rightarrow$ Fe$_2$P $\rightarrow$ Ni$_2$In. However, it is important to emphasize that the Ni$_2$In phase has not been observed yet experimentally for either HfO$_2$ or ZrO$_2$ in contrast to OII and Fe$_2$P phases, likely due to the extreme pressures required to stabilize it.

3.3. Density and volume collapse across transition

Based on our discussion in section 3.1, Ni$_2$In phase is found to be less dense than Fe$_2$P phase at zero pressure and, therefore, is more compressible. However, and due to the high compressibility of Ni$_2$In-HfO$_2$, the calculated volumes for Ni$_2$In are smaller than those of Fe$_2$P at high pressures (Fig. 4). At the transition pressure ($\sim$386 GPa) across Fe$_2$P $\rightarrow$ Ni$_2$In transition, our calculated volume collapse is $\sim$4.4% ($\sim$3.8%) using the second- (third-) order BM-EOS (Fig. 4). This relatively large volume change is expected as this transition is associated with an increase in the CN from 9 to 11. This result compares well with the volume collapse that has been experimentally observed or calculated across OI $\rightarrow$ OII transition in HfO$_2$ and similar dioxides ZrO$_2$ [39] and TiO$_2$ [40], noting that this transition is associated with an increase in the CN from 7 (for OI) to 9 (for OII). However, a very small volume change across OII $\rightarrow$ Fe$_2$P transition has been reported for these dioxides [25–27] as the CN remains unchanged for this transition.
Figure 4: Pressure versus volume of one HfO$_2$ formula unit. The solid line represents the Fe$_2$P phase, whereas the dashed line represents the Ni$_2$In phase. The volume collapse at the transition pressure between the two phases is shown in the inset.

3.4. Hardness estimations
In this section, we discuss the mechanical hardness of our newly predicted Ni$_2$In phase in comparison to the other high-pressure phases of HfO$_2$ and the other similar dioxides that have been expected to have high hardness due to their low compressibility (see Ref. [41]). In fact, it has been recently concluded that this assumption is not valid as none of these phases for these dioxides is qualified to be an ultrahard material. The assumption of Ni$_2$In as being a superhard is refuted by using a scaling model [42].

Based on this model, the hardness is proportional to the average number of bonds per atom, but it is inversely proportional to average atomic volume, coordination number, and bond length [42]. Additionally, the hardness depends on $R_i$, which represents the characteristic length scale of the charge density distribution about each atom. It has been found that $R_i$ is nearly independent of phase [9, 39, 42, 43], where the $R_i$ values using GGA computations [9] are 1.78 Å and 1.07 Å for Hf and O atoms, respectively.

Using this model, we estimated the hardness of Ni$_2$In-HfO$_2$ phase to ~9 GPa, which is ~10% smaller than our recent estimations [25] for the hardness of either OII-HfO$_2$ (9.8 GPa) or Fe$_2$P-HfO$_2$ (10 GPa). This decrease in hardness is expected due to the CN increase and $V_0$ increase in Ni$_2$In compared to OII and Fe$_2$P. Additionally, we should note that the material is called superhard if its hardness exceeds 40 GPa. Consequently, since the estimated hardness for the high-pressure phases of HfO$_2$ is ~9-10 GPa, our general conclusion is that none of these phases is qualified to be superhard.

4. Conclusions
In summary, we tested the high-pressure stability of Ni$_2$In-type phase for HfO$_2$ with respect to Fe$_2$P phase. Our DFT-GGA calculations predicted the transition pressure across Fe$_2$P $\rightarrow$ Ni$_2$In to occur at ~386 GPa with a large volume collapse across the transition of ~4%. Additionally, our computed EOS for the newly predicted phase shows that it is obviously more compressible than Fe$_2$P phase. Finally,
the hardness estimation for Ni$_2$In-HfO$_2$ is consistent with recent studies that have concluded that all known HfO$_2$ polymorphs are not superhard.

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