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Semiconducting phase of hafnium dioxide under high pressure: a theoretical studied by quasi-particle *GW* calculations

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Abstract. The phase stability of the hafnium dioxide compounds HfO_2 , a novel material with a wide range of application due to its versatility and biocompatibility, is predicted to be achievable by using evolutionary technique, based on first-principles calculations. Herein, the candidate structure of HfO_2 is revealed to adopt a tetragonal structure under high-pressure phase with $P4/nmm$ space group. This evidently confirms the stability of the HfO_2 structures, since the decomposition into the component elements under pressure does not occur until the pressure is at least 200 GPa. Moreover, phonon calculations can confirm that the $P4/nmm$ structure is dynamically stable. The $P4/nmm$ structure is mainly attributed to the semiconducting property within using the Perdew–Burke–Ernzerhof, the modified Becke–Johnson exchange potential in combination with the generalized gradient approximations, and the quasi-particle *GW* approximation, respectively. Our calculation manifests that the $P4/nmm$ structure likely to be metal above 200 GPa, arising particularly from *GW* approximation. The remarkable results of this work provide more understanding of the high-pressure structure for designing metal-oxide-based semiconducting materials.

1. Introduction

Hafnium oxide HfO_2 is a remarkable material with various applications. Currently, the Hafnium oxide-based material is mainly used as the ideal memory material, [1, 2, 3, 4, 5] i.e. ferroelectric Si-doped HfO_2 [6, 7, 8, 9] due to its ferroelectric property. Moreover, as a part of solid oxide-deficient technology, HfO_2 is also an attractive material for resistive-switching memories. [10, 11, 12, 13, 14] Under a broad range of pressure, HfO_2 becomes a superhard material. [15, 16, 17] Its physical properties such as structural, electrical, optical and elastic properties has recently been investigated by computational study. [17] Also, HfO_2 is considered an indirect band gap semiconductor with the band gap of 4.62 eV. Therefore, it is expected that HfO_2 could possibly be utilized as metal-oxide-semiconductor devices in the upcoming generations.

Moreover, HfO_2 has been fundamentally studied under high pressure. The phase transition has been demonstrated experimentally by the Raman spectra and x-ray-diffraction technique. [18] As a result, it displayed a monoclinic structure with the space group $P2_1/c$, then transformed into an orthorhombic I with the space group $Pbca$ at 10.2 GPa, and finally at 37 GPa, it transformed into a orthorhombic II with the space group $Pnma$. The structural behavior of the $Pnma$ structure of HfO_2 was investigated at each pressure. [19] It was discovered that the $Pnma$ structure exhibits dynamical stability, but the structure is thermodynamically unstable. The meta stability can be observed up to at least 120 GPa. Additionally, it should be noted that the $Pnma$ structure exhibits semiconductivity with the band gap of 3.36 eV. Interestingly, there is no previous report on the crystal structure of HfO_2 above 120 GPa. Therefore, the existence of a stable structure with novel property of HfO_2 above 120 GPa could be anticipated.

In this work, HfO_2 will be explored by the evolutionary techniques, based on density functional theory, to predict the novel structure as a function of pressure. Following this, the main attention is turned to the prediction of candidate structures under up to 200 GPa of pressure. As a result of the structural prediction, the stability of the candidate structures will be examined by considering the formation enthalpy. From the results, the existence of the structure confirms the composition of binary hafnium oxides, which is HfO_2 , with respect to pure Hf and O. In other words, the material does not decompose into pure elements under at least 200 GPa of pressure. The remarkable result of the evolutionary techniques displayed a candidate high-pressure phase: a tetragonal structure with a space group of $P4/nmm$. By considering the physical properties, the $P4/nmm$ exhibits semiconductivity. These findings provide crucial details for fundamental understanding of the structural behaviour and the electronic properties of the HfO_2 at each pressure. Note also that our work provides only HfO_2 . It is because other Hf-O compounds clearly explores further investigation by Zhang *et.al.*[19].

2. Methods

The computation implemented the Universal Structure Predictor: Evolutionary Xtallography (USPEX) [20] and the Vienna ab initio simulation package (VASP)[21] which utilizes the density functional theory. In all subsequent generations, the random symmetric algorithm employed 40% heredity, 20% random symmetric, 20% soft mutation, and 20% transmutation operators. We then studied the system under the pressure range of 150 to 200 GPa with up to four formula units. There are 1702 configurations which possess the lowest enthalpy in 56 consecutive generations. A convergence test on plane-wave basis set was performed. As a result, the cutoff energy of 700 eV was achieved. This value is used for the formation enthalpy carried on the generalized gradient approximation of the Perdew–Burke–Ernzerhof (GGA-PBE) functional [22]. The projector augmented wave (PAW) method [23] and the conjugate gradient scheme, both implemented in the VASP code,[21] were used for the calculation of the ground state energy. The pseudocore radii of Hf and O are 2.4 Bohr and 1.1 Bohr, respectively, which are small enough to ensure that no overlap of spheres will occur under compressed condition. The tetragonal structure was calculated with an initial Brillouin-zone (BZ) sampling grid of spacing $2\pi \times 0.02 \text{ \AA}^{-1}$ in order to guarantee the convergence of the derived ground-state energy. To confirm the dynamical stability, the structure was calculated by using the *ab initio* lattice dynamics with the supercell approach, as implemented in the VASP code together with the PHONOPY package [24]. As for the density of states, the modified Becke-Johnson (mBJ) exchange potential [25] with the GGA functional was used to fully take into account the energy gap. To further investigate the energy gap, the tetragonal structure was performed a self-energy Σ of a many-body system of electrons, also known as *GW* approximation.[26, 27, 28, 29] One of the well-known *GW* approximation, the technical details of how the *GW* approximation is implemented have been described extensively in Refs [28, 29]. The present work has been calculated within a single-shot calculation (G_0W_0) by neglecting all off-diagonal matrix elements of the self-energy Σ as well as performing a Taylor expansion of the self-energy Σ around the the quasiparticle eigenvalues.

3. Results and discussion

The formation enthalpy of HfO₂ is presented in the convex hulls, as shown in Figure 1, the possibility of HfO₂ existence under compression can be verified. We first investigated the thermodynamic stability from 150 to 300 GPa by using first-principles calculations. It should be noted that our calculations were performed at a temperature of 0 K, indicating that the enthalpy can confirm a phase stability under high pressure. [30, 31, 32, 33, 34, 35, 36, 37] This is due to the fact that there is no entropy contribution. As a result, the relationship between pure elements Hf and O displayed the formation of HfO₂. We considered the compositions of HfO₂, bcc-Hf [38] and C2/m-O. [39] The stability of HfO₂ is presented within the connected lower convex

wrapper, indicating that there is new high-pressure phases found above 150 GPa: the tetragonal structure with the space group of P4/nmm. Considering the pressure of 150 GPa, the aforementioned theoretical findings manifested that the *Pnma* structure is a meta-stable structure, and it is in good agreement with those previously reported by Zhang *et.al.*[19]. Moreover, we further explored the P4/nmm and *Pnma* structures by considering entropy S contribution, which is obtained as

$$S = -k_B \sum_{\nu,q} \ln[1 - \exp(-\hbar\omega_{\nu,q}/k_B T)], \quad (1)$$

where ν and q are band index and the wave vector, respectively. ω is the phonon frequency at ν and q . T is temperature. k_B and \hbar are the Boltzmann constant and the reduced Planck constant, respectively. The relative Gibbs free energy showed that the P4/nmm structure is thermodynamically stable favored over the *Pnma* structure by approximately 0.01 eV at a temperature 300 K and a pressure of 150 GPa. As the temperature is increased, it can see that the the *Pnma* structure is thermodynamically stable at a temperature of 500 K and 1000 K. To understand the structural behavior, it should be noted that the entropy S increased with increasing temperature. We therefore suggested that the *Pnma* structure stable structure depended on the term of $-TS$. Here, we suggested that the *Pnma* structure is a high-temperature phase. The *Pnma* structure, however, beyond the scope of this work, and the issue clearly deserves further investigation –For example, the issue of the dynamical stability at high temperature and electronic properties investigation. Subsequently, the convex hulls showed that the *Pnma* structure is holding the meta-stable structure with respect to the P4/nmm structure. Therefore, it can be implied that the P4/nmm structure is thermodynamically stable and is favored over the *Pnma* by neglecting entropy based on the density functional theory, the formation enthalpy alone is sufficient to confirm phase stability at the temperature of 0 K. Focusing on the P4/nmm structure, the structure is stable up to at least 200 GPa. Interestingly, the new high-pressure structures do not decompose into pure elements up to at least 200 GPa, resulting in the evidence of phase stability in HfO₂.

The possibility of finding an electron in the neighboring space of HfO₂ can be measured by the electron localization function (ELF) [41], as reported in Figure 2, where the structure of HfO₂ is presented as shown in Figure 2 (a). The tendency of ELF in HfO₂ is described by the uniform distribution of electron gas with the same density [31, 32, 42, 43, 44, 45, 46]. For the P4/nmm structure, the calculated ELF reveals a set of chemical bonding at the pressure of 150 GPa. The distances between the first (Hf-O) and second (O-O) nearest neighbors (NN) read 1.9374 Å, and 2.3477 Å, respectively. As a result of the P4/nmm structure, it can be observed that the electron would accumulate around the Hf and O atoms, respectively. It should be noted, however, that the O atoms are not likely to bond.

The dynamical stability of the P4/nmm structure can be confirmed by considering the phonon calculation. We investigated the structures which was obtained from the

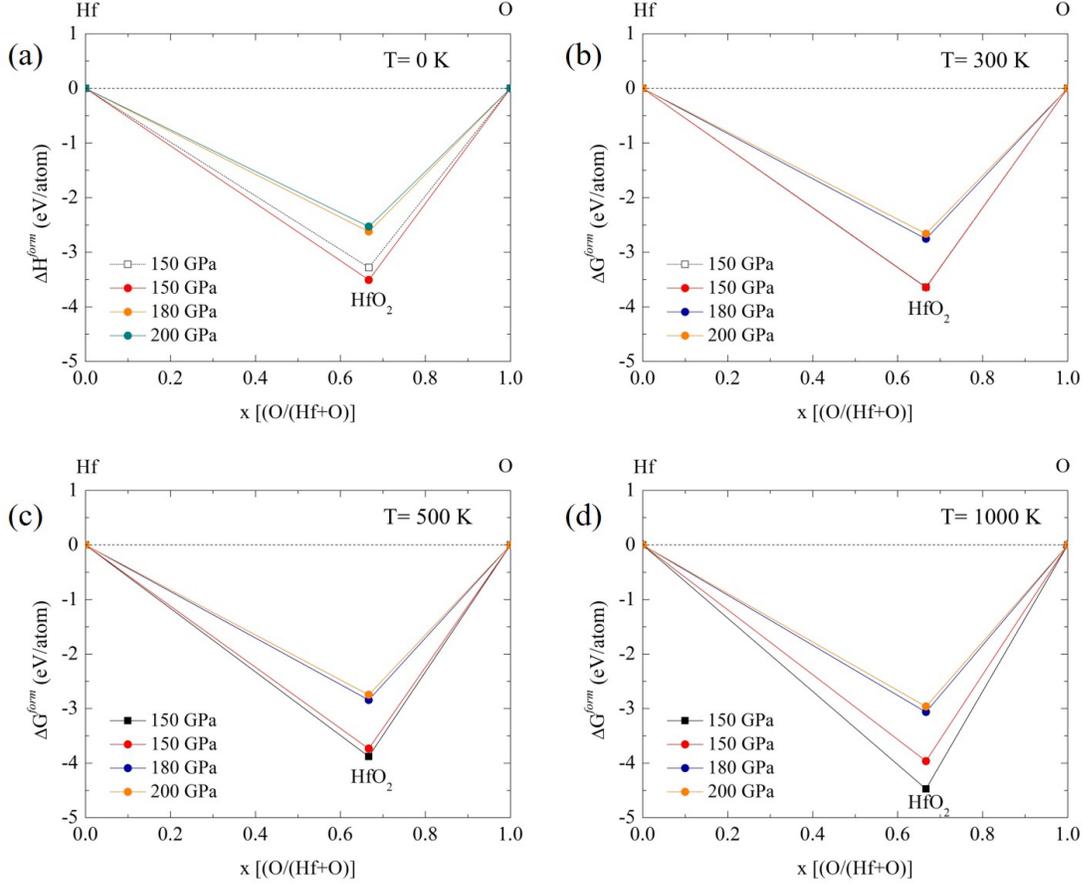


Figure 1. Formation enthalpy and formation Gibbs free energy of HfO_2 as a function of pressure ($150 \text{ GPa} \leq P \leq 200 \text{ GPa}$), as presented in convex hull diagram.

relative enthalpy calculations and discovered that the two new high-pressure structures exhibited negative enthalpies of formation relative to Hf and O; however, it is not enough to a guarantee the thermodynamic stability. As a result, the $P4/nmm$ structure is dynamically stable at a pressure of 150 GPa, as shown in Figure 3. It is because the structures lack the imaginary frequencies that the $P4/nmm$ structure is thermodynamically stable.

We will now discuss electronic property of HfO_2 which is shown in Figure 4, as implemented in the density of states. Here, it can be observed that the $P4/nmm$ structure is semiconductor. Following this, a structural property indicates that, in the PBE method, band gap semiconductors with energy gap of 0.77 eV (Figure 4 (a)). By taking into consideration the fact that the performance of mBJ for the semiconducting property is more accurate as the calculated energy gaps precision would be similar to the hybrid functional, the mBJ method is likely to solution in energy gap of 1.52 eV. By investigating the energy gap, we have chosen to use GW approximation within a single-shot calculation (G_0W_0). At this stage, the G_0W_0 method displayed a large energy gap of 3.05 eV. Therefore, it is mentioned that in the PBE method, the energy gap is

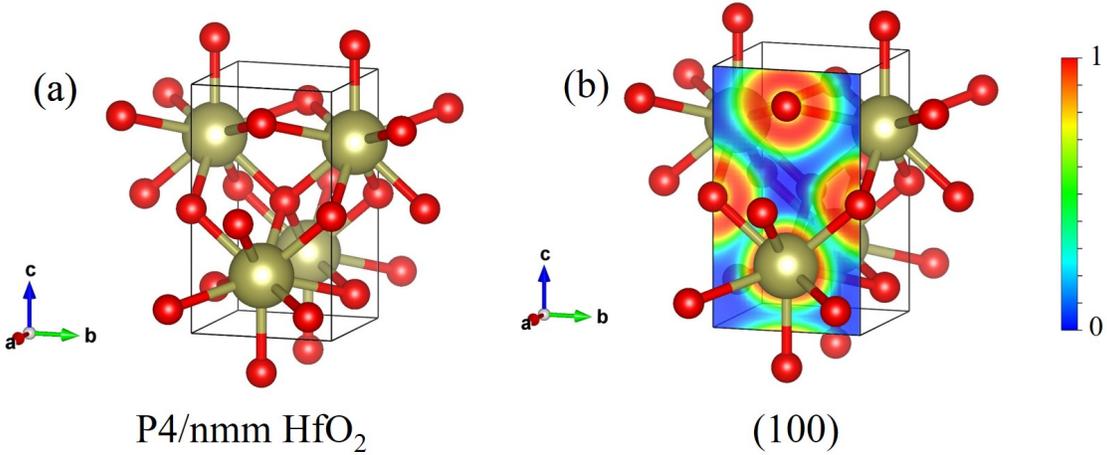


Figure 2. A schematic illustration of HfO_2 : (a) the $P4/nmm$ structure. The gold and red spheres represent, respectively, Hf and O atoms. The electron localization function (ELF) in HfO_2 : (b) ELF of the $P4/nmm$ structure in the (100) atomic plane at 150 GPa (drawn by VESTA (ver. 3.4.7) [40] (URL <https://jip-minerals.org/vesta/en/download.html>)).

likely to be underestimated. With increasing pressure, the PBE method shown that the band gap semiconductors with energy gap of 0.15 eV. Also, the estimated the band gap semiconductors is still large in the $P4/nmm$ structure with energy gap of 1.01 eV by using the mBJ method at a pressure of 200 GPa, as shown in Figure 4 (b). Interestingly, the remarkable result of the G_0W_0 method displayed that the $P4/nmm$ structure is metal because there is electrons occupied at the Fermi level (Figure 4 (b)).

Yet, a more significant change in structural behavior is observed when the pressure increased. As mentioned above, the discovery of apparent metallicity prompts us to further study. It is worth mentioning again that the $P4/nmm$ structure is likely to be metal at a pressure of 200 GPa. Herein, we consider the energy gap as a function of pressure from 150 GPa to 200 GPa. Firstly, the PBE method shown that the estimated energy gap increased gradually from 150 GPa to 180 GPa. Next, the energy gap rose dramatically at a pressure of 190 GPa. After that, the energy gap decreased rapidly at a pressure of 200 GPa. For the case of the mBJ method, the energy gap increased suddenly from 150 GPa to 160 GPa. Then, there was a gradual decrease to 190 GPa, and it decreased suddenly at a pressure of 200 GPa. By employing the G_0W_0 method, our results reveal that, arising particularly from a single-shot calculation, the estimated energy gap decreased gradually from 150 GPa to 170 GPa. Then, we found that it reached a peak of 3.14 eV at a pressure of 180 GPa. After that, the energy gap decreased suddenly from 190 GPa to 200 GPa. These analyses, based on our findings showing the $P4/nmm$ structure accepted to be metallicity above 200 GPa. Consequently, it should be suggested in the sense that it may be possible to obtain a new phase above 200 GPa.

To this end, all of the present work were carried out the first-principle calculation. It is reported to pay a special attention the predicted high-pressure phase with the

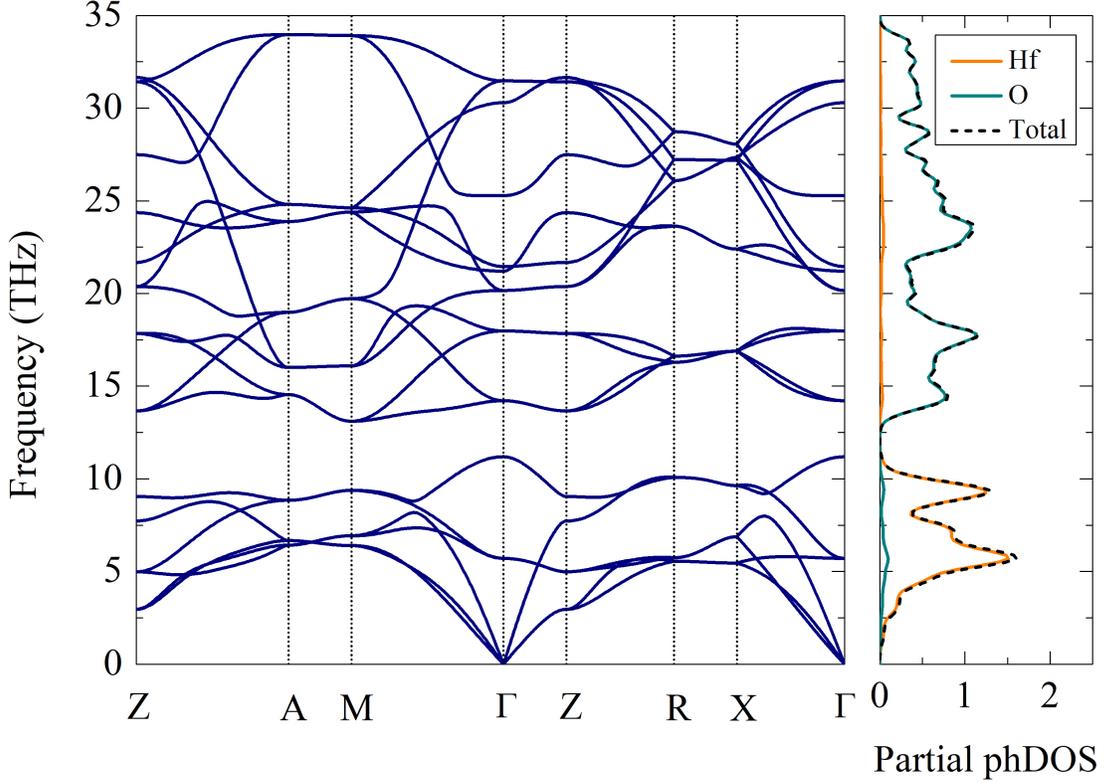


Figure 3. Phonon dispersion curves and the partial phonon density of states of the P4/nmm structure at 150 GPa.

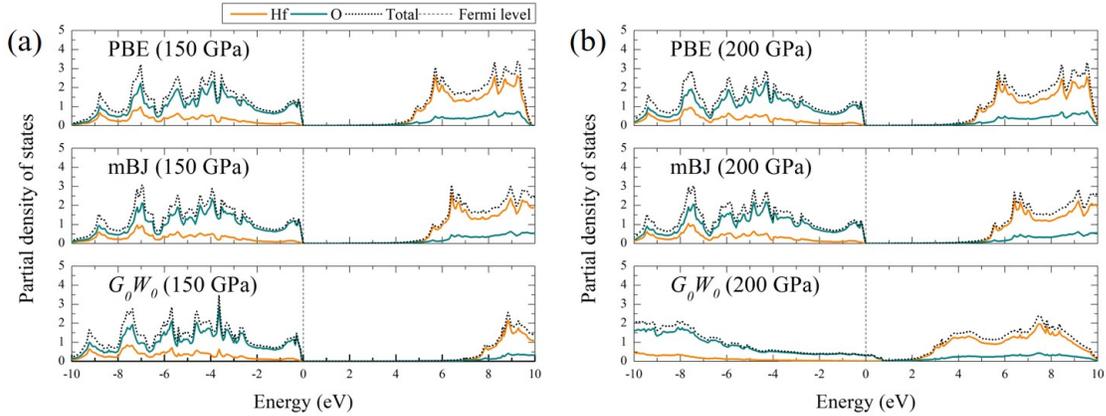


Figure 4. Density of states of the P4/nmm structure: (a) the PBE, the mBJ, and the G_0W_0 are calculated 150 GPa. (b) the PBE, the mBJ, and the G_0W_0 are calculated 200 GPa. The orange and dark cyan represent, respectively, Hf and O atoms.

P4/nmm structure which is predicted to be a semiconductor. We investigated the energy gap as a function of pressure by using the PBE, the mBJ, and the G_0W_0 methods. As results, the calculations pointed out that three methods show a similar trend above a

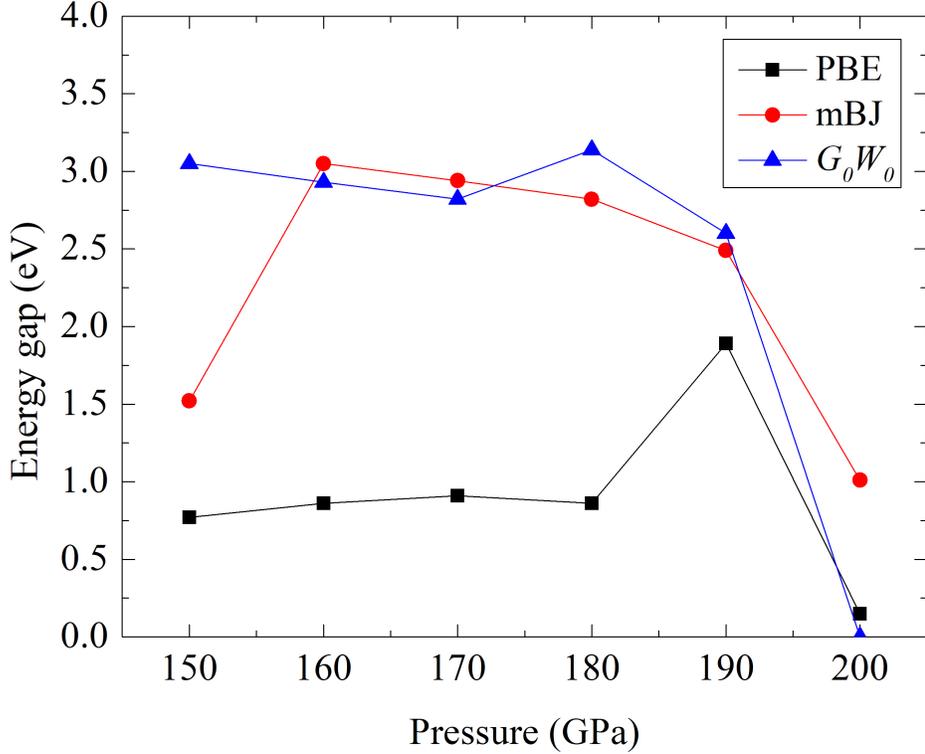


Figure 5. Energy gap of the P4/nmm structure is calculated by the PBE, the mBJ, and the G_0W_0 .

pressure of 190 GPa; however, it should note that the P4/nmm structure is still kept a semiconductor up to at least 190 GPa. Furthermore, the HfO₂ that was investigated in this study would be superior to the metal-oxide-semiconductor devices of the next generation.

4. Conclusion

In summary, the structural behavior of HfO₂ under high pressure demonstrated the stable structures. High pressure phase of hafnium oxides HfO₂ is investigated and compared with those of hafnium and oxygen by using the first-principles calculations, based on the density functional theory, to examine the derived-ground state structure. The original hypothesis of the research, which is that HfO₂ will remain stable rather than decompose under the pressure of up to at least 200 GPa, was evidently confirmed. Our structural predictions have shown that a candidate high-pressure phase is found above 150 GPa: the tetragonal structure with the space group of P4/nmm, as its formation enthalpy lies on the Hf-O convex hull envelopes. HfO₂ displayed physical properties which can be categorized as semiconducting material by using the GGA-PBE method. Following this, the semiconductivity of the P4/nmm structure has been investigated

theoretically, by considering the modified Becke-Johnson (mBJ) exchange potential formalism of the GGA functional and the GW approximation from 150 to 200 GPa. Moreover, the physical origin of semiconductor, based on the quasi-particle G_0W_0 , manifested that the P4/nmm structure is likely to be metal at the pressure of 200 GPa. Our theoretical findings could pave the way for further studies to be conducted in metal oxides and suggests that hafnium oxide could be further investigated experimentally.

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