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## Research Article

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# Electronic topological transitions and mechanical properties of hafnium dioxide allotrope at high pressure: Evolutionary first-principles techniques

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## Abstract

Allotrope of HfO<sub>2</sub> is explored by using first-principles evolutionary algorithm technique, based on density functional theory. The tetragonal structure with a space group of P4/nmm is found to be thermodynamically stable within the harmonic level. Arising particularly from the relative enthalpy, hafnium dioxide allotrope is taken into account in appraising the dynamic stability. Following this, the phonon calculations display that hafnium dioxide allotrope is dynamically stable under compressed conditions. Along with, the density of states suggests that hafnium dioxide allotrope is demonstrated that it is semiconductor. Besides, the more significant change in the shape of density of states is observed when the pressure increased, by adopting an effect of this electronic topological transition, resulting in the energy gap is falling down monotonically. By inspecting their elastic constants and Vicker's

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hardness, the  $P4/nmm$  structure displayed the Vicker's hardness of 26.1 GPa at a pressure of 200 GPa. These findings suggest  $HfO_2$  is more likely to be attained experimentally and theoretically in metal oxides family.

*Keywords:* Hafnium dioxide, structural prediction, semiconductor, mechanical properties, high pressure

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## 1. Introduction

An enhancement of superhard materials aims to go beyond diamond, particularly diamond is the superhard material and is the hardest [1, 2, 3, 4], with a hardness value of 96 GPa by the experimental observation. [2] This fact is well known in diamond is transformed from graphite under compression at a pressure of 15 GPa. [5] In addition to this, it was pointed out that diamond is the crystallography of carbon, and carbon is provided in low- $Z$  elements. [3] Along with, low- $Z$  elements related to low- $Z$  compounds such  $B_4C$ , C-N, SiC, and  $SiO_2$ . At this time, metal oxide is one of the series of materials with hardness materials – for example,  $SiO_2$ ,  $RuO_2$ ,  $AlO_2$ ,  $YO_2$ , and  $ZrO_2$ , respectively.[6]

As already investigated by Chen et al.,[6] it is interesting to note transition metal oxides (TMOs), i.e.,  $RuO_2$ ,  $YO_2$ , and  $ZrO_2$ , respectively. It should be noted that  $RuO_2$  is theoretically reported the Vicker's hardness of 23 GPa. Recently, Mazumder et al., [7] also theoretically calculated Vicker's hardness of  $TiO_2$ ,  $SnO_2$ ,  $ZrO_2$  and  $HfO_2$ , respectively. Following this, it was found that  $HfO_2$  exhibited Vicker's hardness of 11.59 GPa: it has higher than  $TiO_2$ ,  $SnO_2$ , and  $ZrO_2$ . As a result of  $HfO_2$ , it is should mentioned that  $HfO_2$  is notable for hardness property, but also structural behaviour. [7] Also,  $HfO_2$  is considered semiconductor with an indirect band gap, resulting in the band gap of 4.62 eV. This is, therefore,  $HfO_2$  is anticipated to apply as metal-oxide-semiconductor devices in the upcoming generations.

Regarding structural behavior,  $HfO_2$  has been particularly studied under compressed conditions. Without a doubt,  $HfO_2$  has been observed experimentally by the Raman spectra and x-ray-diffraction technique. [8] As a consequence, the ambient phase, which is a monoclinic structure with the space group  $P2_1/c$ , transformed into an orthorhombic I with the space group  $Pbca$  at a pressure of 10.2 GPa. With increasing pressure, it transformed into a or-

thorhombic II with the space group  $Pnma$  at a pressure of 37 GPa. Recently, the crystallography of  $HfO_2$  has been investigated under high pressure.[9] As a result of this, the  $Pnma$  structure is demonstrated that it is a meta-stable because the  $Pnma$  structure is dynamically stable, and it is thermodynamically unstable. Following this, the  $Pnma$  structure is explored the electronic properties, indicating that it is semiconductivity with the band gap of 3.36, eV.

Recently, extensive study of  $HfO_2$  was investigated mechanical properties by the experimental observation. [10] The work has been shown that the  $HfO_2$  exhibited a significant increase in hardness at least up to 14.4 GPa. It is, however, worth to noting that no successful report and attempt to enhance the hardness property of  $HfO_2$  at high pressure. Additionally, the  $Pnma$  structure has been reported by Zhang *et.al.*[9], it is the meta-stable structure. Also, one might think of the  $Pnma$  structure is possible to be a high-temperature phase, if consider an effect of entropy. For this reason, to the best of our knowledge, it might be worth trying to think of allotrope of  $HfO_2$  because it is possible to existence of another meta-stable phase at a temperature of 0 K.

Thus, in this work,  $HfO_2$  is explored by using an evolutionary techniques, based on density functional theory. One of the well-known the Universal Structure Predictor: Evolutionary Xtallography (USPEX). [11], it will be quite intuitive to give an insight into the possible allotrope of  $HfO_2$ . Arising particularly from the relative enthalpy, hafnium dioxide allotrope is taken into account in appraising the stable structure at a temperature of 0 K. Following this, the phonon calculations display that hafnium dioxide allotrope is dynamically stable under compressed conditions. By considering the electronic properties, hafnium dioxide allotrope is demonstrated that it is semiconductor. Regarding hardness properties, we used the Chen model [6] to determine the Vicker harness. Interestingly, these Vicker's harness values are rather high in comparison with those estimated for  $RuO_2$ .

## 2. Computational details

The searching for an allotrope of hafnium oxide compound was performed by first-principles evolutionary techniques, as implemented the Universal Structure Predictor: Evolutionary Xtallography (USPEX). [11] and the Vienna ab initio simulation package (VASP)[12] which utilizes the density functional theory. In all subsequent generations, the random symmetric al-

gorithm employed 40% heredity, 20% random symmetric, 20% soft mutation, and 20% transmutation operators in the pressure range from 150 to 200 GPa with structures containing up to four formula units. All structures were fully relaxed using the generalized gradient approximation of the Perdew–Burke–Ernzerhof (GGA-PBE) functional [13] for the exchange-correlation functional. We employed the projector augmented wave (PAW) method [14] and the conjugate gradient scheme, as implemented in the VASP [12]. 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 extreme 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 [15].

### 3. Results and discussion

As aforementioned in the section of introduction and computational details, we introduce here a allotrope of HfO<sub>2</sub> with high-pressure phase is predicted at high pressure. In present work, our study opens the door to the exploration of the allotrope of HfO<sub>2</sub> above 150 GPa. We have used USPEX to predict the HfO<sub>2</sub> structure under high pressure; the result gave two particularly low-enthalpy structures, indicating that they are a orthorhombic structure and a tetragonal structure with the space group of *Pnma* and the space group of P4/nmm, as shown in Figure 1. Also, the structural details is shown in Table- 1. As a result of this, the structures calculated the relative enthalpy by considering the convex hulls, as shown in Figure 2. Following this, we demonstrated the thermodynamic stability from 150 to 200 GPa by using first-principles calculations, based on density functional theory with the PBE formalism of GGA. At this point, it should be mentioned that our calculations were performed at a temperature of 0 K, indicating that the enthalpy can confirm a phase stability under high pressure. [16, 17, 18, 19, 20, 21, 22, 23] This is due to the fact that there is no entropy contribution. Also, the relationship between pure elements Hf and O indicated the the relative enthalpy of HfO<sub>2</sub>. We considered the compositions of HfO<sub>2</sub>, bcc-Hf [24] and C2/m-O. [25] The stability of HfO<sub>2</sub> is presented within the connected lower convex wrapper, indicating that there is a can-

Table 1: Structures of the HfO<sub>2</sub> at 150 GPa.

Structure	Lattice parameters (Å, °)	Atomic coordinates
Pnma	a = 4.9309 b = 2.9261 c = 5.9259	Hf (0.747, 0.250, 0.123)
	$\alpha = 90 \beta = 90 \gamma = 90$	O (0.355, 0.250, 0.677)
		O (0.966, 0.250, 0.826)
P4/nmm	a = 2.9518 b = 2.9518 c = 5.0428	Hf ( 0.000, 0.500, 0.251)
	$\alpha = 90 \beta = 90 \gamma = 90$	O (0.000, 0.500, 0.862)
		O (0.000,0.000, 0.500)

didate high-pressure phase found above 150 GPa: the tetragonal structure with the space group of P4/nmm. Considering the pressure of 150 GPa, the aforementioned computational 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.*[9]. In fact, our calculations carried out at a temperature of 0 K and this is, however, beyond the scope of this work for consideration at high temperature. We thus propose that the issue clearly deserves further investigation by considering the effect of entropy.

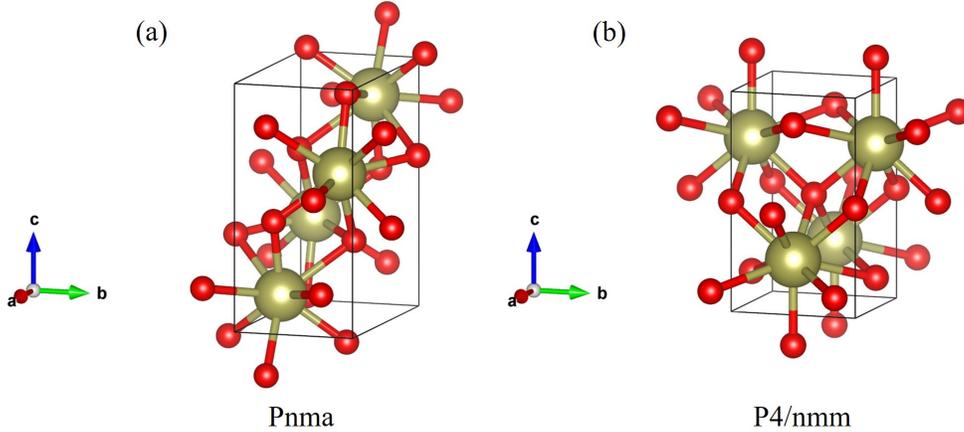


Figure 1: Atomic configurations of the predicted HfO<sub>2</sub> phase (a) the Pnma structure and (b) the P4/nmm structure. Gold and red spheres, respectively, represent Hf and O atoms.

Regarding the dynamically stable structure, we have completed the phonon calculations by considering the P4/nmm structure. According to the aforementioned relative enthalpy findings, one can see that the P4/nmm structure is thermodynamically stable favored over the Pnma structure at a pressure

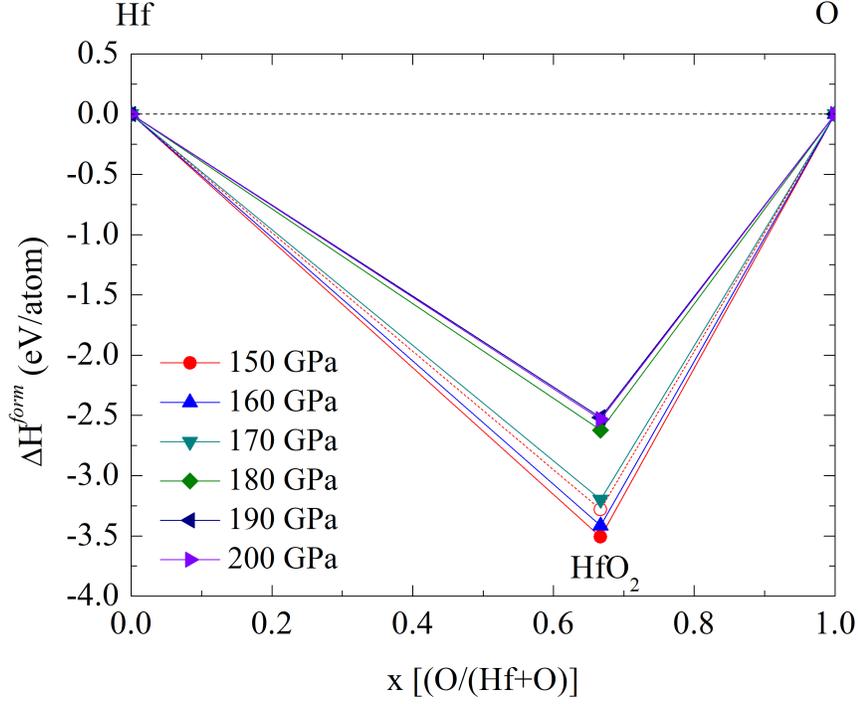


Figure 2: Formation enthalpy of  $\text{HfO}_2$  as a function of pressure, as calculated with respect to hafnium and oxygen, ranging from 150 GPa to 200 GPa.

of 150 GPa. At this point, it is worth to investigate the dynamically stability of the  $P4/nmm$  structure. The remarkable results, we found that the  $P4/nmm$  structure is dynamically stable at a pressure of 150 GPa because it lack an imaginary frequency, as seen in Figure3a. With increasing pressure, the  $P4/nmm$  structure is still dynamically stable at a pressure of 200 GPa. (Figure3b) It is interesting to note that the optical frequencies are significantly higher than that at a pressure of 150 GPa. As a possible cause of this, one might think of the effect of pressure. As a result of this, the  $P4/nmm$  structure will be investigated the electronic and mechanical properties, and is going to be further discussed in the following paragraphs.

To inspect the physical property of the  $P4/nmm$  structure, we considered its density of states (DOS) at each pressure. The results of the DOS are presented in Figure3, where those of Hf and O atoms are also shown for red and dark blue lines, respectively, as well as the total of DOS represents a dot

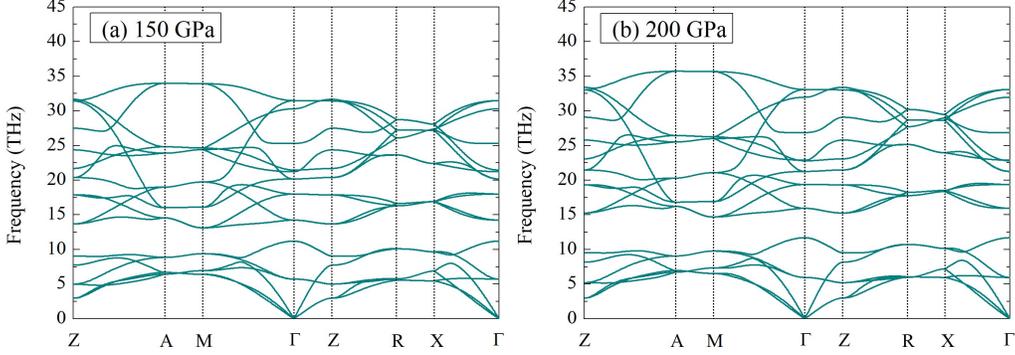


Figure 3: The phonon dispersions of the tetragonal structure (a) at a pressure of 150 GPa and (b) at a pressure of 200 GPa.

line. As a result of this, the P4/nmm structure is a semiconductor, moreover, the DOS displayed the band gap semiconductor with the band gap of 0.77 eV at a pressure of 150 GPa. With increasing pressure, the DOS of the P4/nmm structure exhibited the band gap of the 0.86 eV, in addition, we computed the DOS at a pressure of 180 GPa and found that the P4/nmm structure shown the band gap semiconductor with the band gap of 0.86 eV. Interestingly, the band gap semiconductor of the P4/nmm structure decreased with increasing pressure of 200 GPa, resulting in the estimated the band gap semiconductor with the band gap of 0.15 eV. An observable effect of pressure in the P4/nmm structure is likely to be metallicity. Following this, it should note here that the more significant change in the shape of DOS is observed when the pressure increased. These findings mean that it was first investigated by effect of this electronic topological transition (ETT), indicating that the energy gap was falling down monotonically.

As mentioned above, the P4/nmm structure it is the dynamically stable phases in the absence of imaginary frequency, and it is interesting to demonstrate the mechanical property. At this stage, the P4/nmm structure mainly discussed in an elastic calculation. Here, we demonstrated an elastic stability conditions in the P4/nmm structure, by considering the simplest form of elastic matrix, thus have 6 independent elastic constants [26], which defined as

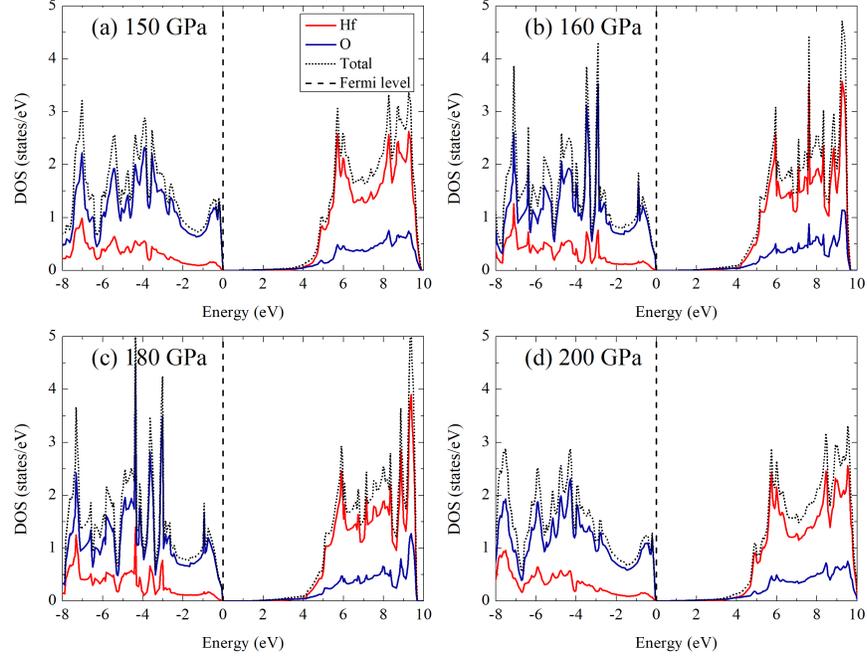


Figure 4: The density of states of the tetragonal structure is calculated at each pressure: (a) 150 GPa, (b) 160 GPa, (c) 180 GPa, and (d) 200 GPa.

$$C_{ij} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & & & \\ \cdot & C_{11} & C_{13} & & & \\ \cdot & \cdot & C_{33} & & & \\ & & & C_{44} & & \\ & & & & C_{44} & \\ & & & & & C_{66} \end{pmatrix}$$

To further understand the mechanical stability criteria, it is theoretically calculated with the following these equations;

$$C_{11} > 0, C_{33} > 0, C_{44} > 0, C_{66} > 0, \quad (1)$$

$$(C_{11} - C_{12}) > 0, (C_{11} + C_{33} - 2C_{13}) > 0, \quad (2)$$

Table 2: Elastic constants as a function of the HfO<sub>2</sub>

Pressure (GPa)	C <sub>11</sub>	C <sub>12</sub>	C <sub>13</sub>	C <sub>33</sub>	C <sub>44</sub>	C <sub>66</sub>
150	1149	606	543	1487	453	318
160	1172	629	557	1519	469	322
170	1199	656	572	1556	486	326
180	1225	683	587	1593	504	329
190	1251	710	602	1628	522	332
200	1277	737	621	1675	539	333

$$[2(C_{11} + C_{12}) + C_{33} + 4C_{13}] > 0. \quad (3)$$

As a result of elastic constants, we found that 6 independent elastic constants displayed all eigenvalues of  $C_{ij}$  are positive, as shown in the Table- 2. Also, the P4/nmm structure is corresponded with two criteria: (i) its phonon modes exhibited positive frequencies for all wave vectors and (ii) the elastic energy displayed always positive. The condition is well-known the elastic stability criterion. By analyzing the elastic property of the P4/nmm structure, we considered the elastic constants as function of pressure. Following, the results shown that the elastic constants increased with increasing pressure, in addition, it should be mentioned that the  $C_{33}$  turned out to be large and it increased gradually from 150 GPa to 200 GPa. Subsequently, it is possible that  $C_{33}$  is a key factor for support the hardness property.

As mentioned hardness property, as first step, we investigated the bulk modulus (B), shear modulus (G), and Young's modulus (E) of the P4/nmm structure by using the relation of elastic constants and calculating the VRH approximation. [27] Secondly, we used the Chen model to determine the Vicker harness as described in Ref. [6]. That is,

$$H_v = 2(k^2G)^{0.585} - 3 \quad (4)$$

This model is described by the empirical formula, based on the Pugh modulus ratio  $k = G/B$ . We computed the Vicker's hardness as a function of pressure. As a result of this, it found that the Vicker's hardness increased significantly from 150 GPa to 200 GPa. These findings tempt one to think of the  $C_{33}$  because this correspondingly results in similarity in the trend of the Vicker's hardness as a function of pressure. We therefore suggested that this evidently confirms the increased Vicker's hardness.

To further understand the hardness properties, we described an electron

Table 3: Calculated Bulk Modulus (B), Shear Modulus (G), Young's Modulus (E), Pugh modulus ratio  $k = G/B$ , and Vickers Hardness ( $H_v$ ), respectively, of the  $\text{HfO}_2$

Pressure (GPa)	B	G	E	G/B	$H_v$
150	796	384	994	0.482	24.7
160	816	393	1017	0.481	25.0
170	839	403	1043	0.480	25.3
180	862	413	1069	0.479	25.7
190	884	423	1094	0.478	26.0
200	910	432	1120	0.475	26.1

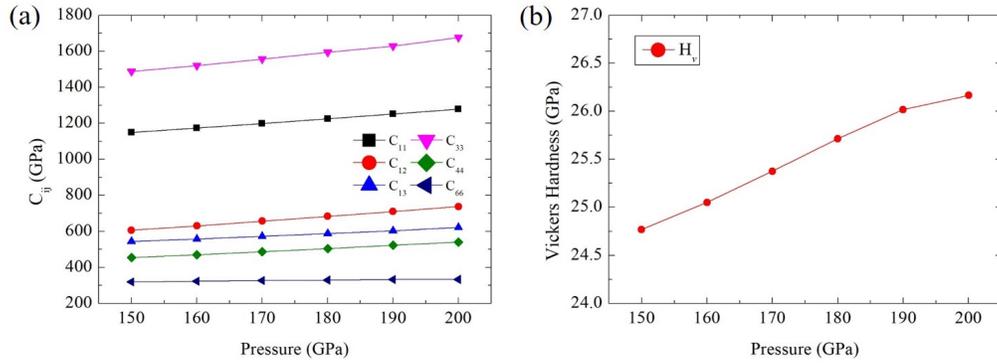


Figure 5: (a) Elastic constants of tetragonal structure as a function of pressure and (b) Vicker hardness of as a function of pressure.

in the neighboring space of  $\text{HfO}_2$  can be obtained by the electron localization function (ELF) [28], as reported in the (101) plane, where the structure of  $\text{HfO}_2$  is presented as shown in Figure 6. For the  $P4/nmm$  structure, the calculated ELF reveals a set of chemical bonding at the pressure of 150 GPa, by adopting the uniform distribution of electron gas with the same density [17, 18, 29, 30, 31, 32, 33]. The distances between the first (Hf-O) and second (O-O) nearest neighbors (NN) read 1.937 Å, and 2.347 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. Also, with increasing pressure up to 200 GPa, it is found that the distances between the first (Hf-O) and second (O-O) NN read 1.912 Å, and 2.307 Å, respectively. It should be noted, moreover, that the O atoms are likely to very weak bond. Nevertheless, it is worth noting that electrons at a pressure of 200 GPa are

slightly accumulated higher than at a pressure of 150 GPa, as can be seen in red circle dot (Figure 6). As a result of this, one might think that the nature of electrons accumulated the first (Hf-O) NN supports the increased Vicker's hardness.

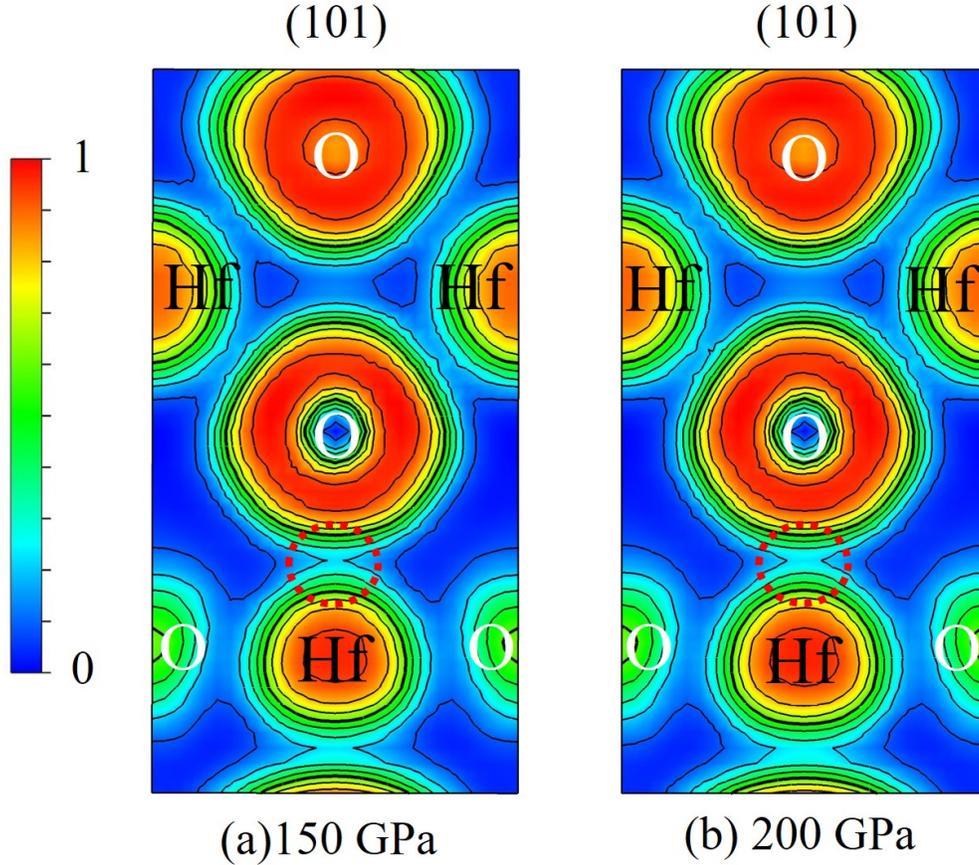


Figure 6: The electron localization function (ELF) in  $\text{HfO}_2$ : (a) ELF of the  $P4/nmm$  structure in the (101) atomic plane at 150 GPa and (b) ELF of the  $P4/nmm$  structure in the (101) atomic plane at 200 GPa (drawn by VESTA (ver. 3.4.7) [34] (URL <https://jp-minerals.org/vesta/en/download.html>)).

#### 4. Conclusion

In summary, we have performed the first-principles evolutionary techniques to predict an allotrope of  $\text{HfO}_2$  at high pressure. Regarding the

structural predictions, we find an orthrhombic structure and a tetragonal structure with the space group of  $Pnma$  and the space group of  $P4/nmm$ . The remarkable result of the relative enthalpy shows that the  $P4/nmm$  structure is thermodynamically favored over the  $Pnma$  structure at a pressure of 150 GPa. Apart from this, the  $P4/nmm$  structure is dynamically stable. This evidently is conformed by the phonon calculations. Along with, the density of states suggests that hafnium dioxide allotrope is semiconductor. Following this, it finds that the energy gap is falling down monotonically, by adopting an effect of this electronic topological transition, resulting in the more significant change in the shape of DOS is observed when the pressure increased. By inspecting its Vicker's harness, the  $P4/nmm$  structure displayed the Vicker's harness of 26.1 GPa at a pressure of 200 GPa.

## 5. acknowledgement

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