

First-Principles Study of Dynamical and Dielectric Properties of Orthorhombic Phases of Group IVb Transition Metal Oxides

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Using density-functional theory, we investigate the structural, vibrational and dielectric properties of the orthorhombic phases of the group IVb transition metal dioxides (HfO_2 , ZrO_2 , TiO_2). We discuss the Born effective charge tensors, the phonon frequencies at the Γ point of the Brillouin zone, and the dielectric permittivity tensors.

Introduction

For several decades, silicon dioxide has been used as the gate dielectric in metal-oxide-semiconductor (MOS) transistors. With the continuous reduction of their size, the thickness of the gate dielectric has steadily decreased in order to increase the gate capacitance and thereby the drive current and the device performance. Below 2 nm thickness, leakage currents appear due to direct tunneling through the oxide, leading to increased power consumption and reduced device reliability. Therefore, further size reduction of MOS transistors requires the replacement of the SiO_2 gate dielectric with a material of higher permittivity in order to maintain a small gate leakage current (1). Considerable research efforts have been dedicated to the study of potential dielectric-gate materials.

The group IVb transition metal (Hf, Zr, Ti) metal oxides stand among the most promising candidates to replace SiO_2 . Indeed, these materials have shown much promise (1). On the one hand, the TiO_2 system is attractive due to its anomalously high permittivity (2, 3, 4, 5). On the other hand, HfO_2 and ZrO_2 in the form of amorphous films are stable in direct contact with Si up to high temperature, which is highly desirable to avoid the degradation of the interface properties by formation of a low-k interfacial layer (6).

The dynamical (Raman and infrared vibrational frequencies) and dielectric properties of the various crystalline forms of HfO_2 , ZrO_2 , and TiO_2 constitute an issue of great practical relevance, which has stimulated a series of first-principles investigations (7, 8, 9, 10, 11). First, the tetragonal phase of ZrO_2 was considered (7) and compared to the cubic phase, which had been studied previously for other reasons (12, 13). The study of the monoclinic phase of ZrO_2 (8) completed nicely the analysis of crystalline Zr oxides. Similar studies were also performed for crystalline HfO_2 (9, 11) and TiO_2 (10). In this paper, we extend these previous works by performing a thorough study of the orthorhombic phases of HfO_2 , ZrO_2 and TiO_2 that have been observed at high-pressure (14, 15, 16, 17) or in thin films (18, 19). Note that the dielectric constants of the orthorhombic phases of HfO_2 and ZrO_2 have also been calculated (20).

The present paper is organized as follows. The technical details are described briefly in the first section. The structural parameters of the O-I and O-II phases of HfO_2 , ZrO_2 , and

TiO₂ are discussed in the second section. The corresponding Born effective charge tensors, the phonon frequencies at the Γ point of the Brillouin zone are presented in the third and fourth sections, respectively. The respective dielectric permittivity tensors are analyzed in detail in the fifth section. Finally, we summarize our results and conclude.

Technical Details

All our calculations are performed using the ABINIT package, developed by the authors and collaborators (21). The exchange-correlation energy is evaluated within the local density approximation to density-functional theory, using Perdew-Wang's parameterization (22) of Ceperley-Alder electron-gas data (23).

Only valence electrons are explicitly considered using pseudopotentials to account for core-valence interactions. We use norm-conserving pseudopotentials (24, 25). The parameters used to generate the pseudopotentials are reported in Table I. We adopt a separable form for the pseudopotentials (26) treating the following angular-momentum waves as local: f for Hf, d for Zr, d for Ti, and p for O.

TABLE I. Pseudopotentials parameters for the different atomic species: levels treated as valence states, reference configuration, and corresponding core radii (r in a.u.) taken for describing the various angular waves (s , p , d , and f).

Atom	Valence states	Reference configuration	r_s	r_p	r_d	r_f
Hf	$5s, 5p, 5d, 6s$	$5s^2 5p^6 5d^2 6s^2$	1.50	2.85	2.45	3.50
Zr	$4s, 4p, 4d, 5s$	$4s^2 4p^6 4d^2 5s^0$	1.75	1.55	1.70	
Ti	$3s, 3p, 3d, 4s$	$3s^2 3p^6 3d^2 4s^0$	1.25	1.25	1.65	
O	$2s, 2p$	$2s^2 2p^4$	1.50	1.50		

The wavefunctions are expanded in plane waves up to a kinetic energy cutoff of 30 Ha. The Brillouin zone is sampled by Monkhorst-Pack grids (27). For the O-I phase, we use a $2 \times 4 \times 4$ mesh that leads to 4 special k -points in the irreducible Brillouin zone; while, for the O-II phase, we adopt a $4 \times 6 \times 3$ mesh that results in 12 special k -points. The chosen kinetic energy cutoff and k -point sampling of the Brillouin zone ensure convergence of all the calculated properties.

Linear response properties such as the Born effective charge tensors or the phonon frequencies are obtained as second-order derivatives of the total energy with respect to an external electric field or to atomic displacements. These second-order derivatives are calculated within a variational approach to density-functional perturbation theory (28, 29, 30). parameters as for the calculation of the ground state properties.

Structural Properties

The O-I phase (space group $Pbca$, N^o 61) of HfO₂, ZrO₂, and TiO₂ has an orthorhombic unit cell which contains 8 formula units of MO₂ with M=(Hf, Zr, Ti). All the atoms occupy 8c Wyckoff sites (x, y, z) with parameters x , y , and z specified for M atoms and two non-equivalent oxygen atoms O1 and O2. The atoms of type O1 are threefold coor-

dinated, while O2 are fourfold coordinated. All M atoms are equivalent and are sevenfold coordinated. Three lattice-vector parameters (a , b , and c) and nine internal parameters are needed to fully specify the structure. Our calculated structural parameters for the O-I phase of HfO₂, ZrO₂, TiO₂ are reported in Table II. Our results are in good agreement with previous theoretical calculations (15, 17).

TABLE II. Structural parameters for the O-I and O-II phases of of HfO₂, ZrO₂, and TiO₂. The length unit is the Å. The volume per formula unit V is given in Å³.

		HfO ₂			ZrO ₂			TiO ₂		
O-I	a b c	10.14	5.30	5.11	9.94	5.20	4.88	9.17	4.88	4.70
	M	(0.885	0.034	0.254)	(0.885	0.035	0.254)	(0.886	0.043	0.253)
	O1	(0.792	0.377	0.128)	(0.792	0.378	0.132)	(0.791	0.380	0.143)
	O2	(0.977	0.739	0.497)	(0.977	0.739	0.497)	(0.972	0.737	0.495)
O-II	a b c	5.61	3.32	6.57	5.50	3.27	6.41	5.18	3.03	6.05
	M	(0.246	0.250	0.115)	(0.246	0.250	0.114)	(0.243	0.250	0.117)
	O1	(0.359	0.250	0.427)	(0.359	0.250	0.427)	(0.359	0.250	0.427)
	O2	(0.026	0.750	0.337)	(0.026	0.750	0.337)	(0.027	0.750	0.340)

The O-II phase (space group $Pnma$, N° 62) of HfO₂, ZrO₂, and TiO₂ has an orthorhombic unit cell which contains 4 formula units of MO₂ with M=(Hf, Zr, Ti). All the atoms occupy 4c Wyckoff sites ($x, \frac{1}{4}, z$) with parameters x and z specified for M atoms and two non-equivalent oxygen atoms O1 and O2. The atoms of type O1 are fourfold coordinated, while O2 are fivefold coordinated. All M atoms are equivalent and are ninefold coordinated. Three lattice-vector parameters (a , b , and c) and six internal parameters are needed to fully specify the structure. Our calculated structural parameters for the O-II phase of HfO₂, ZrO₂, TiO₂ are reported in Table II. Our results are in good agreement with previous theoretical calculations (15).

Born Effective Charge Tensors

In Table III, we report the calculated Born effective charge tensors of M=(Hf, Zr, Ti) and O atoms in the two phases of hafnia, zirconia, and titania. Due to the symmetry of the O-II phase, the xy and yx components of the Born effective charge tensors vanish for all atoms. The principal values of the symmetric part of the tensors are also given in Table III.

In both phases, the principal values of Z^* are anomalously large for M=(Hf, Zr, Ti) atoms compared to the nominal ionic charge $Z=+4$, indicating a mixed covalent-ionic bonding (31). The same observation holds for the O1 and O2 atoms for which the nominal ionic charge is $Z=-2$. On average, the principal values of Z^* are slightly larger in the O-I phase. Note also that the anisotropy of the Born effective charge tensors is less pronounced for the O-II phase, the highest anisotropy being encountered for the O1 atoms in the O-I phase with a ratio between the largest and smallest components of about 2.6, 2.8 and 3.5 for HfO₂, ZrO₂, and TiO₂, respectively.

Turning to the comparison between hafnia, zirconia, and titania, it appears that the Born effective charges are very similar in HfO₂ and ZrO₂ while the difference are noticeable with

TABLE III. Calculated Born effective charge tensors of M=(Hf, Zr, Ti) and for the two types of O atoms in the O-I and O-II phases of HfO₂, ZrO₂, and TiO₂. The principal values of the symmetric part of the tensors are also indicated between brackets.

		HfO ₂	ZrO ₂	TiO ₂
O-I	M	$\begin{pmatrix} 5.50 & -0.03 & 0.27 \\ -0.42 & 5.33 & 0.05 \\ 0.03 & 0.14 & 4.99 \end{pmatrix}$	$\begin{pmatrix} 5.68 & 0.01 & 0.31 \\ -0.44 & 5.48 & 0.03 \\ 0.04 & 0.14 & 5.07 \end{pmatrix}$	$\begin{pmatrix} 6.01 & 0.16 & 0.52 \\ -0.78 & 6.06 & -0.06 \\ 0.04 & 0.16 & 4.80 \end{pmatrix}$
		[5.66 5.27 4.89]	[5.83 5.42 4.98]	[6.36 5.78 4.73]
		O1	$\begin{pmatrix} -2.98 & 0.97 & 0.60 \\ 0.79 & -2.55 & 0.34 \\ 0.67 & 0.34 & -2.46 \end{pmatrix}$	$\begin{pmatrix} -3.08 & 1.09 & 0.64 \\ 0.87 & -2.64 & 0.35 \\ 0.67 & 0.35 & -2.49 \end{pmatrix}$
	[-3.75 -2.84 -1.43]		[-3.93 -2.87 -1.41]	[-4.59 -2.78 -1.32]
	O2		$\begin{pmatrix} -2.52 & -0.01 & 0.03 \\ -0.04 & -2.78 & 0.36 \\ 0.08 & 0.32 & -2.53 \end{pmatrix}$	$\begin{pmatrix} -2.60 & -0.01 & 0.02 \\ -0.05 & -2.84 & 0.38 \\ 0.11 & 0.32 & -2.58 \end{pmatrix}$
		[-2.52 -3.02 -2.29]	[-2.60 -3.09 -2.33]	[-2.68 -3.23 -2.27]
O-II		M	$\begin{pmatrix} 4.99 & 0.00 & 0.22 \\ 0.00 & 4.97 & 0.00 \\ 0.07 & 0.00 & 5.13 \end{pmatrix}$	$\begin{pmatrix} 5.05 & 0.00 & 0.20 \\ 0.00 & 5.02 & 0.00 \\ 0.12 & 0.00 & 5.19 \end{pmatrix}$
	[4.90 4.97 5.22]		[4.95 5.02 5.29]	[4.71 4.83 5.12]
	O1		$\begin{pmatrix} -2.38 & 0.00 & 0.25 \\ 0.00 & -2.31 & 0.00 \\ 0.21 & 0.00 & -2.80 \end{pmatrix}$	$\begin{pmatrix} -2.40 & 0.00 & 0.24 \\ 0.00 & -2.36 & 0.00 \\ 0.21 & 0.00 & -2.85 \end{pmatrix}$
		[-2.28 -2.31 -2.90]	[-2.31 -2.36 -2.94]	[-2.06 -2.11 -2.86]
		O2	$\begin{pmatrix} -2.61 & 0.00 & 0.14 \\ 0.00 & -2.67 & 0.00 \\ 0.01 & 0.00 & -2.33 \end{pmatrix}$	$\begin{pmatrix} -2.64 & 0.00 & 0.09 \\ 0.00 & -2.66 & 0.00 \\ -0.03 & 0.00 & -2.35 \end{pmatrix}$
	[-2.63 -2.67 -2.31]		[-2.64 -2.66 -2.35]	[-2.72 -2.72 -2.19]

respect to TiO₂ with the the following global trend: $Z^*(\text{HfO}_2) \leq Z^*(\text{ZrO}_2) \leq Z^*(\text{TiO}_2)$. For the metal atoms, titania presents the largest principal values in the O-I phase (up to 10% larger in TiO₂ than in ZrO₂) while in the O-II phase the differences between HfO₂, ZrO₂, and TiO₂ are smaller (at most 4%). For the oxygen atoms, the difference in the Born effective charges are also a few percent at the noticeable exception of the O1 atoms in the O-I phase (already pointed out) for which the principal values can be up to 17% larger in titania compared to zirconia.

Phonon Frequencies at the Γ Point

The theoretical group analysis predicts the following irreducible representations of optical and acoustical zone-center modes for the O-I phase:

$$\Gamma_{\text{O-I}} = \underbrace{9A_g \oplus 9B_{1g} \oplus 9B_{2g} \oplus 9B_{3g}}_{\text{Raman}} \oplus \underbrace{8B_{1u} \oplus 8B_{2u} \oplus 8B_{3u}}_{\text{IR}} \oplus \underbrace{9A_u}_{\text{Silent}} \oplus \underbrace{B_{1u} \oplus B_{2u} \oplus B_{3u}}_{\text{Acoustic}}$$

and for the O-II phase:

$$\Gamma_{\text{O-II}} = \underbrace{6A_g \oplus 3B_{1g} \oplus 6B_{2g} \oplus 3B_{3g}}_{\text{Raman}} \oplus \underbrace{5B_{1u} \oplus 2B_{2u} \oplus 5B_{3u}}_{\text{IR}} \oplus \underbrace{3A_u}_{\text{Silent}} \oplus \underbrace{B_{1u} \oplus B_{2u} \oplus B_{3u}}_{\text{Acoustic}}$$

Due to the non-vanishing components of the Born effective charge tensors, the dipole-dipole interaction leads to the splitting at the Γ point between the longitudinal and transverse optic (LO and TO, respectively) modes B_{1u} , B_{2u} , and B_{3u} in both phases. Our calculated phonon frequencies and symmetry assignments are reported in Tables IV and V.

TABLE IV. Fundamental frequencies (in cm^{-1}) of the O-I phase of HfO_2 , ZrO_2 , and TiO_2 with their symmetry assignments. The superscript (m or o) indicates the atoms (metal or oxygen) whose motion dominates in the vibrational mode.

	Mode	HfO ₂	ZrO ₂	TiO ₂	Mode	HfO ₂	ZrO ₂	TiO ₂	Mode	HfO ₂	ZrO ₂	TiO ₂	
Raman	A _g (1)	109.0	141.0	173.3	A _g (2) ^m	135.3	189.4	242.5	A _g (3)	186.7	209.1	277.1	
	A _g (4)	252.1	328.4	320.7	A _g (5)	334.4	352.8	358.6	A _g (6)	382.6	371.2	443.2	
	A _g (7)	434.8	429.3	486.0	A _g (8)	564.3	564.4	614.7	A _g (9)	616.0	614.8	671.6	
	B _{1g} (1) ^m	127.8	178.0	207.6	B _{1g} (2) ^m	156.4	217.8	310.9	B _{1g} (3) ^m	214.2	289.7	330.8	
	B _{1g} (4)	288.6	313.0	404.5	B _{1g} (5) ^o	428.1	430.7	465.3	B _{1g} (6) ^o	466.8	454.1	468.3	
	B _{1g} (7)	567.3	576.5	639.1	B _{1g} (8) ^o	651.0	655.3	713.6	B _{1g} (9)	679.8	690.0	748.8	
	B _{2g} (1) ^m	138.5	195.9	259.1	B _{2g} (2) ^m	166.2	226.1	291.2	B _{2g} (3) ^m	196.0	267.2	309.3	
	B _{2g} (4)	296.3	313.8	348.5	B _{2g} (5) ^o	339.2	341.5	392.2	B _{2g} (6) ^o	455.7	454.1	486.4	
	B _{2g} (7)	495.1	491.7	552.9	B _{2g} (8)	574.5	577.8	624.3	B _{2g} (9)	770.6	801.8	880.2	
	B _{3g} (1) ^m	111.2	152.2	193.2	B _{3g} (2) ^m	127.3	174.6	248.5	B _{3g} (3)	245.9	269.6	330.6	
	B _{3g} (4)	247.0	330.5	338.0	B _{3g} (5)	348.0	355.3	440.6	B _{3g} (6) ^o	488.2	484.2	521.2	
	B _{3g} (7)	563.9	563.6	598.6	B _{3g} (8)	603.4	616.1	668.2	B _{3g} (9) ^o	694.1	700.8	740.5	
	Silent	A _u (1) ^m	88.4	119.6	153.6	A _u (2) ^m	132.9	176.6	226.4	A _u (3) ^m	146.8	206.3	279.4
		A _u (4)	292.6	315.1	363.7	A _u (5)	388.0	391.2	424.5	A _u (6)	425.6	433.4	466.9
		A _u (7)	512.7	505.1	525.2	A _u (8)	576.0	576.5	639.8	A _u (9)	716.6	731.9	806.0
Infrared	B _{1u} (TO1)	177.0	184.5	227.3	B _{1u} (TO2)	190.5	256.0	283.7	B _{1u} (TO3)	217.1	288.6	340.6	
	B _{1u} (LO1)	188.2	206.3	252.2	B _{1u} (LO2)	194.3	256.0	284.4	B _{1u} (LO3)	222.9	289.6	353.8	
	B _{1u} (TO4)	349.0	352.0	377.3	B _{1u} (TO5)	373.6	372.8	437.5	B _{1u} (TO6)	426.9	428.4	465.1	
	B _{1u} (LO4)	353.0	355.2	377.3	B _{1u} (LO5)	417.0	410.3	450.6	B _{1u} (LO6)	543.7	545.8	582.0	
	B _{1u} (TO7)	568.3	563.2	596.0	B _{1u} (TO8)	636.0	663.1	712.5					
	B _{1u} (LO7)	635.6	662.9	708.6	B _{1u} (LO8)	660.4	694.6	727.7					
	B _{2u} (TO1) ^m	127.0	176.3	228.3	B _{2u} (TO2) ^m	186.2	255.1	325.0	B _{2u} (TO3)	259.0	279.0	335.6	
	B _{2u} (LO1)	127.0	176.4	228.4	B _{2u} (LO2)	186.4	257.3	327.6	B _{2u} (LO3)	291.0	306.6	368.6	
	B _{2u} (TO4)	395.2	396.2	429.2	B _{2u} (TO5)	412.9	419.4	448.8	B _{2u} (TO6) ^o	475.7	470.0	506.3	
	B _{2u} (LO4)	407.4	407.3	446.9	B _{2u} (LO5)	467.7	466.8	500.7	B _{2u} (LO6)	590.2	590.7	593.0	
	B _{2u} (TO7)	612.8	608.4	628.2	B _{2u} (TO8)	677.6	692.3	750.2					
	B _{2u} (LO7)	660.3	680.4	746.8	B _{2u} (LO8)	715.5	751.2	825.1					
	B _{3u} (TO1)	80.3	104.2	120.9	B _{3u} (TO2)	244.1	263.9	297.3	B _{3u} (TO3)	250.1	321.4	320.4	
	B _{3u} (LO1)	81.5	106.2	123.8	B _{3u} (LO2)	244.2	297.7	305.0	B _{3u} (LO3)	302.8	335.2	355.4	
	B _{3u} (TO4)	346.9	357.0	363.7	B _{3u} (TO5)	390.0	397.4	453.6	B _{3u} (TO6)	417.3	427.2	523.1	
	B _{3u} (LO4)	348.0	371.9	444.5	B _{3u} (LO5)	417.3	426.6	506.5	B _{3u} (LO6)	492.4	486.8	533.5	
	B _{3u} (TO7)	519.3	517.2	578.8	B _{3u} (TO8)	714.8	728.0	788.5					
	B _{3u} (LO7)	623.1	650.8	692.2	B _{3u} (LO8)	770.1	802.7	881.4					

It is very interesting to compare the phonon frequencies calculated for HfO_2 , ZrO_2 , and TiO_2 . There are several possible origins for the variations that are observed between Hf, Zr,

TABLE V. Fundamental frequencies (in cm^{-1}) of the O-II phase of HfO_2 , ZrO_2 , and TiO_2 with their symmetry assignments. The superscript (m or o) indicates the atoms (metal or oxygen) whose motion dominates in the vibrational mode.

	Mode	HfO ₂	ZrO ₂	TiO ₂	Mode	HfO ₂	ZrO ₂	TiO ₂	Mode	HfO ₂	ZrO ₂	TiO ₂
Raman	A _g (1) ^m	118.3	171.8	222.5	A _g (2) ^m	175.8	248.1	334.9	A _g (3) ^o	364.1	367.2	399.6
	A _g (4) ^o	443.3	447.2	482.0	A _g (5) ^o	574.5	581.7	650.0	A _g (6) ^o	620.3	634.2	706.1
	B _{1g} (1) ^m	125.6	181.1	250.7	B _{1g} (2) ^o	379.7	384.0	413.2	B _{1g} (3) ^o	599.9	612.5	674.3
	B _{2g} (1)	215.8	294.7	359.4	B _{2g} (2)	255.7	349.4	430.0	B _{2g} (3)	386.1	399.6	492.1
	B _{2g} (4)	533.4	551.8	597.8	B _{2g} (5) ^o	560.1	566.6	607.8	B _{2g} (6) ^o	665.4	677.9	734.8
	B _{3g} (1) ^m	109.8	159.2	242.4	B _{3g} (2) ^o	410.4	415.0	444.1	B _{3g} (3) ^o	605.4	619.0	674.5
Silent	A _u (1)	82.7	123.9	184.3	A _u (2)	322.1	324.2	337.9	A _u (3)	489.5	497.5	542.3
Infrared	B _{1u} (TO1)	139.2	186.0	223.9	B _{1u} (TO2)	285.8	322.5	394.0	B _{1u} (TO3)	419.4	438.6	498.2
	B _{1u} (LO1)	153.6	210.8	260.6	B _{1u} (LO2)	345.1	363.2	420.3	B _{1u} (LO3)	531.2	555.4	600.2
	B _{1u} (TO4) ^o	612.8	620.9	674.3	B _{1u} (TO5) ^o	628.6	643.3	691.4				
	B _{1u} (LO4)	624.5	639.4	675.0	B _{1u} (LO5)	708.5	743.2	789.5				
	B _{2u} (TO1)	291.6	307.5	351.0	B _{2u} (TO2)	541.7	555.3	607.4				
	B _{2u} (LO1)	481.8	491.6	517.4	B _{2u} (LO2)	634.5	678.9	713.6				
	B _{3u} (TO1)	178.9	221.6	264.9	B _{3u} (TO2)	323.2	378.0	434.8	B _{3u} (TO3)	387.3	403.4	474.5
	B _{3u} (LO1)	202.7	258.2	319.3	B _{3u} (LO2)	361.4	397.8	462.7	B _{3u} (LO3)	510.8	515.0	568.7
	B _{3u} (TO4) ^o	518.2	525.0	585.6	B _{3u} (TO5) ^o	692.8	707.2	738.6				
	B _{3u} (LO4)	610.8	657.4	676.4	B _{3u} (LO5)	695.0	710.6	744.0				

and Ti oxides: structural changes (e.g. the volume), change of the mass ratio $\text{Hf/Zr}=1.96$ and $\text{Zr/Ti}=1.90$, and differences in interatomic force constants.

The structural changes reported in Table II are not very big, in particular between hafnia and zirconia. We suspect that their effect should not be the most important origin for the variations observed in the phonon frequencies. In order to check this, we compute the phonon frequencies for hafnia and titania assuming that the interatomic force constants are the same as those for zirconia, while the volume is allowed to vary. In hafnia, we find that the frequencies are decreased by 2% on average (at most 8%) in both O-I and O-II phases; where as in titania, they are increased by 4% and 3% on average (at most 13% and 7%) in the O-I and O-II phases, respectively. This analysis shows that the structural changes play a relatively minor role in agreement with our intuition. Their effect is slightly more important in titania since the structural changes are larger.

As for the role of the mass ratio, it is interesting to focus on the modes in which the $M=(\text{Hf, Zr, Ti})$ atoms are not much involved (indicated by the superscript o in Tables IV and V) and on those in which on the contrary the $M=(\text{Hf, Zr, Ti})$ atoms move significantly more than O atoms (indicated by the superscript m in Table IV and V). In the former case, the phonon frequencies should not be affected very much by the change between Hf, Zr, or Ti; whereas, in the latter case the variation should be very important. In both phases, there are no modes in which the metal atoms are fixed by symmetry.

For the modes in which the $M=(\text{Hf, Zr, Ti})$ atoms are not much involved (indicated by the superscript o in Tables IV and V), we observe indeed that the phonon frequencies do

not vary very much between hafnia and zirconia, indicating the interatomic forces are very similar in these materials. In contrast, the phonon frequencies in titania differ significantly from those in hafnia and zirconia indicating that the differences in the interatomic force constants are important.

For the modes in which the M=(Hf, Zr, Ti) atoms move significantly more than O atoms (indicated by the superscript m in Tables IV and V), it is also possible to evidence the influence of the interatomic force constants. For this purpose, we compute the phonon frequencies for hafnia and titania assuming that the interatomic force constants are the same as those for zirconia, while the mass of the metal atom is changed to that of Hf or Ti. These simple calculations lead to frequencies which are reduced by roughly 28% for hafnia and increased by about 34% for titania with respect to zirconia. When these results compare well with those of Tables IV and V, it can be considered that the effect of the interatomic force constants is negligible. This is actually what we find in all cases for hafnia compared to zirconia in both O-I and O-II phases. For the comparison between titania and zirconia, it is only true for the modes $B_{2g}(1)$ and $A_u(3)$ in the O-I phase and the mode $A_g(2)$ in the O-II phase, indicating once more significant differences in the interatomic force constants.

In conclusion, while the interatomic force constants in hafnia and zirconia are very similar, they differ considerably in titania. As a result, while the differences in the phonon frequencies in Hf and Zr oxides can mostly be explained by the ratio between the masses of the two metals, the most important origin for the variation in Ti oxides is the interatomic force constants.

Dielectric Permittivity Tensors

In both phases, the electronic (ϵ_∞) and static (ϵ_0) permittivity tensors are diagonal. They have three independent components ϵ_{xx} , ϵ_{yy} and ϵ_{zz} . In Table VI, the calculated values of ϵ_∞ and ϵ_0 are reported for the O-I and the O-II phases of hafnia, zirconia, and titania. The dielectric constants are larger in the O-II phase: the average values of ϵ_∞ and ϵ_0 are roughly 10% larger (in ZrO_2 , the average value of ϵ_0 is only 5% larger in the O-II phase, and in TiO_2 it is 15% larger).

In the O-I, the average value of ϵ_∞ (ϵ_0) is 7% (15%) smaller in hafnia than in zirconia and 45% (43%) larger in titania than in zirconia. In the O-II, the average value of ϵ_∞ (ϵ_0) is 6% (6%) smaller in hafnia than in zirconia and 47% (18%) larger in titania than in zirconia. Like for the frequencies at Γ (see discussion of the fourth section), the dielectric constants in hafnia and in zirconia are quite similar while they differ significantly in titania. This difference is less pronounced in the O-II phase.

In order to analyze the static dielectric tensors, we can rely not only on the frequencies of the IR-active modes, but also on the corresponding eigendisplacements and Born effective charges. Indeed, the static dielectric tensor can be decomposed in the contributions of different modes as follows (see Ref. (32); we follow the notations of Ref. (30)):

$$\epsilon_{\alpha\beta}^0(\omega) = \epsilon_{\alpha\beta}^\infty + \sum_m \Delta\epsilon_{m,\alpha\beta} = \epsilon_{\alpha\beta}^\infty + \frac{4\pi}{\Omega_0} \sum_m \frac{S_{m,\alpha\beta}}{\omega_m^2}, \quad [1]$$

where Ω_0 is the volume of the primitive unit cell and $S_{m,\alpha\beta}$ the mode-oscillator strength,

TABLE VI. Electronic and static dielectric tensors for of the O-I and O-II phases of HfO₂, ZrO₂, and TiO₂. The contributions of the different phonon modes to the static dielectric tensor are also indicated. The tensors are diagonal but they have different components in the three directions parallel. The phonon mode contributions to ϵ_0^{xx} , ϵ_0^{yy} , and ϵ_0^{zz} come from the IR-active B_{3u}, B_{2u}, and B_{1u} modes, respectively.

		HfO ₂			ZrO ₂			TiO ₂		
		<i>xx</i>	<i>yy</i>	<i>zz</i>	<i>xx</i>	<i>yy</i>	<i>zz</i>	<i>xx</i>	<i>yy</i>	<i>zz</i>
O-I	ϵ_∞	5.30	5.17	5.05	5.68	5.53	5.35	8.31	8.43	7.23
	$\Delta\epsilon_1$	0.70	0.01	3.27	1.08	0.04	4.98	2.04	0.02	5.67
	$\Delta\epsilon_2$	0.22	0.04	0.15	9.75	0.96	0.01	8.87	3.48	0.09
	$\Delta\epsilon_3$	9.13	5.29	0.64	1.89	5.00	0.18	13.78	8.21	2.01
	$\Delta\epsilon_4$	0.14	4.67	1.38	1.94	4.31	1.40	0.00	9.79	0.00
	$\Delta\epsilon_5$	5.09	1.88	5.69	3.71	4.20	6.00	0.56	1.00	4.24
	$\Delta\epsilon_6$	0.01	0.50	1.00	0.08	0.35	2.29	0.18	0.63	4.04
	$\Delta\epsilon_7$	0.62	0.17	0.27	1.05	0.25	0.32	1.64	1.16	0.35
	$\Delta\epsilon_8$	0.30	0.06	0.00	0.36	0.06	0.00	0.72	0.03	0.01
	ϵ_0	21.52	17.78	17.45	25.53	20.69	20.53	39.08	32.74	23.63
O-II	ϵ_∞	5.87	5.75	5.88	6.21	6.08	6.23	9.19	8.93	9.19
	$\Delta\epsilon_1$	6.36	15.16	4.57	8.41	16.21	6.28	11.89	16.44	8.25
	$\Delta\epsilon_2$	7.28	0.63	7.52	7.39	0.94	5.21	5.92	1.40	3.37
	$\Delta\epsilon_3$	3.24		3.32	1.81		4.39	1.98		4.76
	$\Delta\epsilon_4$	0.12		0.59	0.27		0.78	0.39		0.00
	$\Delta\epsilon_5$	0.01		0.19	0.01		0.16	0.04		1.23
		ϵ_0	22.88	21.54	22.06	24.11	23.22	23.05	29.41	26.77

which can be expressed in terms of the eigendisplacements and the Born effective charge tensors by:

$$S_{m,\alpha\beta} = \left(\sum_{\kappa\alpha'} Z_{\kappa,\alpha\alpha'}^* U_m^*(\kappa\alpha') \right) \left(\sum_{\kappa'\beta'} Z_{\kappa',\beta\beta'}^* U_m(\kappa'\beta') \right). \quad [2]$$

Displacements are normalized thanks to the condition

$$\sum_{\kappa\beta} M_\kappa [U_m(\kappa\beta)]^* U_n(\kappa\beta) = \delta_{mn}, \quad [3]$$

where M_κ is the mass of the ion κ .

The contribution of the individual modes $\Delta\epsilon_m$ to the static dielectric constants, as defined in Eq. [1], are presented in Table VI.

In parallel to this decomposition of the static dielectric tensor, one can define a mode-effective charge vector:

$$Z_{m,\alpha}^* = \frac{\sum_{\kappa\beta} Z_{\kappa,\alpha\beta}^* U_m(\kappa\beta)}{\left(\sum_{\kappa\beta} U_m^*(\kappa\beta) U_m(\kappa\beta) \right)^{\frac{1}{2}}}. \quad [4]$$

In Table VII, we present for each IR-active mode, the magnitude of its mode-effective charge vectors (this vector is parallel to the z , y , and x axis for the B_{1u}, B_{2u}, and B_{3u} modes, respectively), as well as the relevant component of the oscillator strength tensor (the zz component for B_{1u} modes, the yy component for B_{2u} modes, and the xx component for the B_{3u} modes).

TABLE VII. Components of mode-effective charge vectors Z_m^* and oscillator strength tensor S_m for each of the IR-active modes of the O-I and O-II phases of HfO₂, ZrO₂, and TiO₂. The description of the reported vector and tensor components corresponding to the different modes is given in the text. The components of the mode-effective charge vectors are given in units of $|e|$, where e is the electronic charge. The oscillator strengths are given in 10^{-4} a.u. (1 a.u.=0.342036 m³/s²).

		HfO ₂		ZrO ₂		TiO ₂	
		Z_m^*	S_m	Z_m^*	S_m	Z_m^*	S_m
O-I	B _{1u} (1)	3.37	3.14	3.89	4.89	4.61	6.86
	B _{1u} (2)	1.61	0.16	0.35	0.02	0.80	0.16
	B _{1u} (3)	3.14	0.93	1.98	0.43	4.51	5.45
	B _{1u} (4)	3.97	5.16	3.90	5.01	0.04	0.00
	B _{1u} (5)	8.72	24.32	9.32	24.06	9.64	19.00
	B _{1u} (6)	4.10	5.56	6.29	12.10	8.99	20.49
	B _{1u} (7)	2.81	2.63	2.97	2.93	2.98	2.89
	B _{1u} (8)	0.21	0.01	0.15	0.01	0.50	0.07
	B _{2u} (1)	0.41	0.01	0.67	0.03	0.38	0.02
	B _{2u} (2)	1.01	0.04	3.96	1.80	6.74	8.60
	B _{2u} (3)	5.85	10.86	6.51	11.22	9.02	21.66
	B _{2u} (4)	8.32	22.32	7.91	19.50	12.24	42.23
	B _{2u} (5)	5.43	9.81	8.21	21.33	3.99	4.70
	B _{2u} (6)	3.18	3.45	2.56	2.24	3.34	3.76
	B _{2u} (7)	2.40	1.96	2.80	2.65	5.66	10.73
	B _{2u} (8)	1.57	0.85	1.55	0.82	1.06	0.38
	B _{3u} (1)	1.41	0.14	1.66	0.34	1.91	0.70
	B _{3u} (2)	2.24	0.40	8.22	19.58	7.95	18.36
	B _{3u} (3)	8.03	17.49	5.84	5.62	11.10	33.15
	B _{3u} (4)	1.26	0.53	4.76	7.14	0.01	0.00
	B _{3u} (5)	8.68	23.71	7.99	16.88	3.09	2.71
	B _{3u} (6)	0.45	0.06	1.26	0.43	2.75	1.17
	B _{3u} (7)	3.87	5.09	4.90	8.10	6.22	12.86
	B _{3u} (8)	3.72	4.73	4.01	5.46	5.58	10.46
O-II	B _{1u} (1)	3.67	1.21	4.05	2.79	4.18	4.38
	B _{1u} (2)	5.59	8.36	5.74	6.95	5.41	5.55
	B _{1u} (3)	5.00	7.96	6.01	10.86	6.63	12.53
	B _{1u} (4)	2.98	3.00	3.39	3.84	0.00	0.00
	B _{1u} (5)	1.72	1.01	1.56	0.83	4.36	6.23
	B _{2u} (1)	7.61	17.56	8.32	19.68	8.79	21.47
	B _{2u} (2)	2.74	2.52	3.36	3.72	4.16	5.47
	B _{3u} (1)	4.70	2.77	4.98	5.30	5.74	8.84
	B _{3u} (2)	6.75	10.36	8.47	13.56	6.29	11.87
	B _{3u} (3)	4.54	6.62	3.65	3.79	5.38	4.71
	B _{3u} (4)	1.14	0.44	1.69	0.96	2.06	1.42
	B _{3u} (5)	0.47	0.08	0.47	0.08	0.78	0.20

The largest contribution $\Delta\epsilon_m$ to ϵ_0 is by far that of the B_{2u}(1) mode in the O-II phase. Indeed, it is the only mode that combines both a large oscillator strength ($S_m \sim 20 \times 10^{-4}$ a.u.) and a relatively low frequency ($\omega_m \sim 300 - 350$ cm⁻¹).

The frequency factor in Eq. [1] plays a crucial role. For instance, let us compare the B_{1u}(1) mode and the B_{2u}(4) mode in the O-I phase of TiO₂. The latter has an oscil-

lator strength about 6 times larger than the former ($S_m \sim 40 \times 10^{-4}$ a.u. to be compared with $S_m \sim 7 \times 10^{-4}$ a.u.) but at the same time its frequency is about twice larger ($\omega_m \sim 430 \text{ cm}^{-1}$ to be compared with $\omega_m \sim 230 \text{ cm}^{-1}$) for the former. As a result, its contribution to the dielectric constant is only 1.7 times larger.

It is difficult to observe a systematic trend when comparing hafnia, zirconia, and titania. However, we note that for most of the modes the oscillator strengths and the mode-effective charges essentially increase from HfO₂ to ZrO₂ and from ZrO₂ to TiO₂ (as a counterexample, the B_{1u}(2) mode in the O-II phase presents just the opposite trend). This can be related to the behavior of the Born effective charges $Z_{\kappa,\alpha\alpha'}^*$ and the eigendisplacements $U_m(\kappa\alpha)$, the two quantities that appear in the definitions of $S_{m,\alpha\beta}$ and $Z_{m,\alpha}^*$ given in Eqs. [2] and [4]. On the one hand, as discussed in the third section, the Born effective charges show globally the following trend: $Z^*(\text{HfO}_2) \leq Z^*(\text{ZrO}_2) \leq Z^*(\text{TiO}_2)$. On the other hand, the displacements of Hf atoms are smaller than those of Zr atoms, which in turn are smaller than those of Ti atoms, simply because the mass increases from Ti to Hf (as discussed in the fourth section). If one now considers the contributions to the static dielectric constant reported in Table VI, it appears that $\Delta\epsilon(\text{HfO}_2) \leq \Delta\epsilon(\text{ZrO}_2) \leq \Delta\epsilon(\text{TiO}_2)$ for almost all of the modes.

Conclusion

Using density-functional theory, we have investigated the structural, electronic, dynamical, and dielectric properties of the O-I and O-II phases of HfO₂, ZrO₂ and TiO₂. The parameters of the relaxed atomic structures are found to be in very good agreement with previous theoretical studies (when available).

The Born effective charge tensors have been calculated showing an important anisotropy. For some directions, these effective charges are found to be larger than the nominal ionic charge, indicating a mixed covalent-ionic bonding between M=(Hf, Zr, Ti) and O atoms. We have also discussed the effective charges focusing on the changes between the systems containing hafnium, zirconium, and titanium.

The phonon frequencies at the center of the Brillouin zone have been computed. Differences between the vibrational frequencies of Hf, Zr, and Ti compounds have been rationalized in terms of changes in the structural parameters, difference in mass between Hf, Zr, and Ti, and variations in the interatomic force constants.

The electronic and static dielectric permittivity constants have been computed, and a detailed analysis of the contributions of individual vibrational modes has been performed, including the computation of mode-effective charges and oscillator strengths.

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