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Ab initio study of mechanical and thermo-acoustic properties of tough ceramics: applications to HfO₂ in its cubic and orthorhombic phase

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Abstract

By means of the *ab initio* all-electron new full-potential linear-muffin-tin orbitals method, calculations were made for elastic constants C_{11} , C_{12} and C_{44} for Si, ZrO₂ and HfO₂ in their cubic phase, and constants C_{11} , C_{22} , C_{33} , C_{12} , C_{13} , C_{23} , C_{44} , C_{55} and C_{66} for HfO₂ in its orthorhombic phase. Using the Voigt and Reuss theory, estimations were made for polycrystals of their bulk, shear and Young moduli, and Poisson coefficients. The speed of elastic wave propagations and Debye temperatures were estimated for polycrystals built from Si and the above mentioned compounds. The semicore 4f¹⁴ electrons should be included in the valence set of Hf atom in this all-electron approach if accurate results for elastic properties under pressures are looked for.

1. Introduction

Ceramics such as HfO₂ and ZrO₂ are oxides that have raised considerable interest in research and technology sectors during the past two decades due to their excellent dielectric properties and structural stability. Even though the normal phase is monoclinic $P2_1/c$, by the addition of Y₂O₃ [1] it is possible to stabilize a solid solution that contains a mixture of tetragonal and cubic phases, while in powders with sizes smaller than 60 nm it is stable in the tetragonal and below 2 nm in the cubic phase.

Application of pressures to the normal phase $P2_1/c$ allows the transition between the orthorhombic OI ($Pbca$) and orthorhombic OII ($Pnma$) phases. When the applied pressures exceed 30 GPa [15] the OI → OII transformation is irreversible, with a stabilized $Pnma$ phase with bulk moduli B between 312 and 335 GPa, values that exceed by approximately 80 GPa the normal phase value of $B = 233$ GPa. This latter process is known as hardening.

By applying temperature, phases with tetragonal ($P4_2nmc$) and cubic ($Fm\bar{3}m$) structures are obtained [1]. The elastic properties of solids are important because they provide information on interatomic interaction potentials and thus on fundamental properties of the solid state. These constants are also related thermodynamically to specific heat and thermal expansion. The elastic properties determine the response of the crystal to externally applied forces, and therefore define the bulk modulus, shear modulus, Young modulus and the Poisson coefficient for the material.

Pugh [2] introduced the ratio between bulk and shear modulus, B/G , for polycrystalline phases as a means to measure the ductile/brittle ratio in metals. A high (low) value of the ratio B/G is associated with ductility (brittleness). Efforts made to calculate the elastic constants of these materials in their different phases have been relatively scarce. The major difficulty in calculating such elastic constants through *ab initio* methods lies in the fact that significant accuracy is required in total bulk energy calculation and having the ability to solve with precision the small variations in such energies (of the order of 1/10 mRyd per atom of the

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compound) while being subjected to uniaxial, biaxial and shear deformations, all of which are in the linear range.

2. Theoretical methodology

The elastic stiffness constant C_{ij} define the hardness of a crystal when an external tension is applied. For small deformations (isothermic) it is expected that the elastic energy (energy of the deformed crystal minus the energy of the undeformed crystal) presents a quadratic dependence with the tensor of the deformation (Hooke's law) [3]. The elastic constant C_{ij} tensor is represented (in abbreviated form) by means of a 6×6 square matrix, with 36 components. Due to the symmetry of the tensor ($C_{ij} = C_{ji}$), the maximum number of independent components is reduced to 21, applicable to cases involving triclinic crystals, the sole symmetry operation being the identity [4]. For other crystals with greater symmetry, the number of independent constants is reduced even further. For the extreme case of highly symmetric crystals with cubic symmetry (such as Si in the diamond structure and the structure for fluorite), the number of independent constants is reduced to three (C_{11} , C_{12} , C_{44}) [3] and for crystals with orthorhombic structures, the number of elastic constants is nine (C_{11} , C_{22} , C_{33} , C_{12} , C_{13} , C_{23} , C_{44} , C_{55} , C_{66}) [4–6].

The elastic energy per unit volume of arbitrary deformed crystal, as a function of the deformations u_i , is expressed in the following way [3], [7]:

$$U = \frac{1}{2} C_{ij} u_i u_j \quad (1)$$

where $U = (E - E_0)$ is the elastic deformation energy per unit volume, C_{ij} , u_i are the components of the tensor of the elastic constants and of the strain tensor, respectively. Note that the subscripts of the equations (1) are in the notation presented by Voigt [8], in which the labels 1, 2, 3, 4, 5 and 6 replace xx , yy , zz , yz , xz and xy , respectively. Keeping in mind what has been presented up until now, and applying crystal symmetry operations, the elastic energy U for cubic crystals (in our case, the $Fm\bar{3}m$ fluorite structure) takes the form

$$U = \frac{1}{2} C_{11} (u_1^2 + u_2^2 + u_3^2) + C_{12} (u_1 u_2 + u_1 u_3 + u_2 u_3) + 2C_{44} (u_4^2 + u_5^2 + u_6^2) \quad (2)$$

and for orthorhombic crystals (here, the $Pnma$ symmetry) the energy is

$$U = \frac{1}{2} (C_{11} u_1^2 + C_{22} u_2^2 + C_{33} u_3^2) + C_{12} u_1 u_2 + C_{13} u_1 u_3 + C_{23} u_2 u_3 + 2(C_{44} u_4^2 + C_{55} u_5^2 + C_{66} u_6^2). \quad (3)$$

The new full-potential linear-muffin-tin orbitals (NFP-LMTO) *ab initio* method [9], based on smooth Hankel functions [10] and on the local density functional theory (LDA) [11, 12], is used for the calculation of total energies for crystals with or without deformations. All calculations were developed including three atoms in the $Fm\bar{3}m$ (fluorite) cubic cell and 12 atoms in the $Pnma$ (cotunnite) cell. The atomic positions for each strained structure were relaxed by minimizing the atomic force components through solving damped movement equations by means of viscous friction coefficients [13, 14].

Wavefunctions for Hf and O were optimized individually in order to obtain total energies that converge in a few mRyd/atom, taking as an example Hf in the oxide monoclinic structure. The valence electronic configurations of the atomic species were $6s^2, 5d^2, 4f^{14}$ for Hf, $2s^2, 2p^4$ for oxygen, and $5s^2, 5d^2$ for Zr. Note that we included the $4f^{14}$ electrons of the Hf atom. Following the pseudopotential literature on HfO_2 , using the NFP-LMTO method we have first-principles calculated the structural and elastic properties, including these 4f electrons in the core: while the equilibrium lattice constant was right, we obtained a large disagreement in the bulk modulus, about double the experimental value, 332 GPa [15]. Agreement with the experimental bulk modulus, B , is found only when these 4f electrons are included in the valence set. Although the 4f electrons appear as a narrow band, it seems that in our all-electron method they play a role in the interatomic forces of the oxide, mainly when the bonds are stretched/compressed (two-body terms). Previous to this work, we developed a detailed *ab initio* study of all known HfO_2 phases [16] using the pseudopotential-LDA based SIESTA code, and found that, if the 4f electrons are included in the core and utilizing Troullier–Martins pseudopotentials with nonlinear corrections for the core–valence electron interactions, not only do calculated structural and elastic properties show agreement with experiments, but also the transition pressures between normal and high pressures phases. [16]

In the cubic $Fm\bar{3}m$ structure, after obtaining the equilibrium volume, deformations of approximately $\pm 2\%$ relative to this range were performed; the criteria utilized to perform such deformations in cubic crystals are those presented in [17]. To determine the elastic constants for orthorhombic HfO_2 , a series of deformations defined by u_1 , u_2 and u_3 and their combinations were applied to the crystal. In each run, all atomic positions in the cell are relaxed until atomic forces lower than $0.01 \text{ eV } \text{\AA}^{-1}$ are achieved. In this manner, all values for elastic energy U , a product of the deformations, were least-squares adjusted by means of the following equation:

$$U = \frac{1}{2} (C_{11} u_1^2 + C_{22} u_2^2 + C_{33} u_3^2) + C_{12} u_1 u_2 + C_{13} u_1 u_3 + C_{23} u_2 u_3. \quad (4)$$

From the adjustments made, the values for the elastic constants C_{11} , C_{22} , C_{33} , C_{12} , C_{13} and C_{23} were obtained as well as the equilibrium lengths for the cell axes. It is important to note that although the calculations for these elastic constants could have been achieved separately by performing volume conserving u_i deformations in different directions and by conducting adjustments in such curves to the energy equation [17], it was found that the procedure of simultaneous deformations and later adjustment to the energy equation is the most adequate for these cases [18].

In order to calculate the elastic constants C_{44} , C_{55} and C_{66} in the OII structure, each C_{ij} was individually calculated applying the corresponding shear deformation: u_4 for the determination of C_{44} , u_5 for C_{55} and u_6 for C_{66} , all of them in the linear regime.

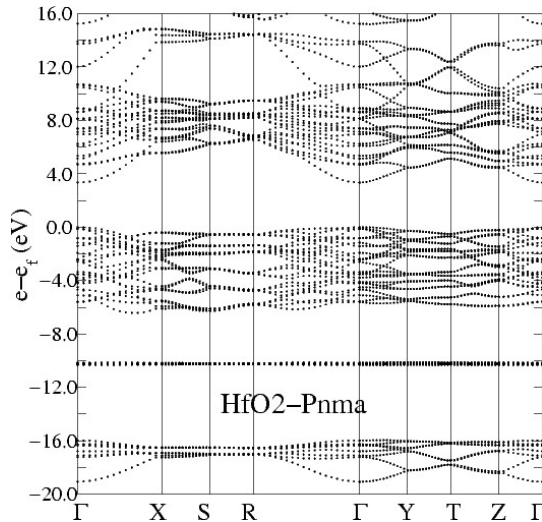


Figure 1. *Pnma*-HfO₂ band-structure along Brillouin zone high symmetry directions.

3. Results and discussions

In figure 1 we show the band-structure of HfO₂ in the cotunnite structure, along high symmetry directions of the Brillouin zone. The valence band has a 19 eV band-width, a value which coincides with previous calculations made with first-principles pseudopotentials [16, 31]. Above the bottom band (composed by oxygen s-electrons) and located at -10 eV below the Fermi level (top of the valence band), we found a narrow band which corresponds to the 4f-Hf electrons. The width of this narrow band is about 0.2 eV. The minimum band gap is located at Γ , corresponding to a direct transition, and has a width of 3.7 eV, higher than the 2.85 eV value we calculated with the SIESTA code [16]. This increase is assigned to a different treatment of core electrons. Figure 2 shows the total density of states per formula unit for HfO₂-*Pnma*. The methodology used by other authors in determining the elastic constants is usually based on the simultaneous application of uniaxial deformations combined in such way that the volume of the crystal is maintained constant [17]. Since the present work is based on the application of uniaxial and biaxial deformations which imply variations in volume, we have verified the previously described method by applying it first to the diamond structure of Si (semiconductor), an element that has been widely characterized experimentally and theoretically. Table 1 shows the elastic constant results. The agreement with experiments is excellent; we found an improvement in the precision of the C_{11} , C_{12} values for Si hereby obtained with respect to reference theoretical values by Nielsen–Martin [19] found in the literature. We hence extended the method in the calculations of constants corresponding to ZrO₂ and HfO₂ in the cubic and orthorhombic phases.

With these values for the elastic constants of single crystals it is possible to calculate useful elastic properties for polycrystals using the Voigt [8] and Reuss [20] approximations. These approaches are for upper and lower

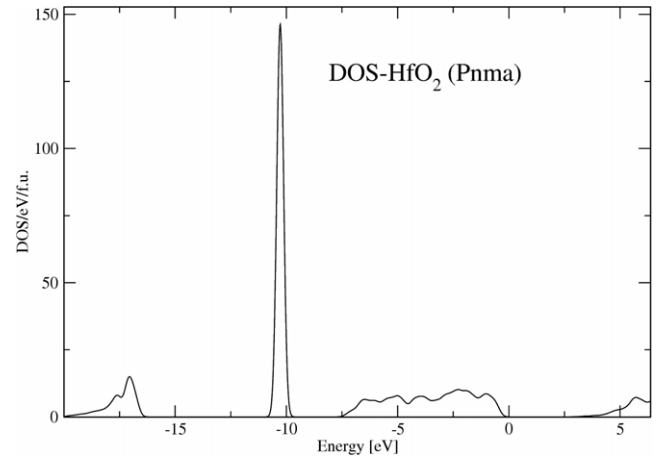


Figure 2. *Pnma*-HfO₂ total density of states with the energy scale relative to the top of the valence band. The narrow peak located at -10 eV corresponds to Hf 4f electrons.

Table 1. Elastic constants calculated for Si-diamond structure ZrO₂ and HfO₂ in the *Fm3m* cubic phase, compared with available experimental and theoretical values obtained by other research groups. Experimental values for ZrO₂ and HfO₂ are extrapolated to zero porosity ($Pp = 0$). All units are in GPa.

Material	C_{11}	C_{12}	C_{44}
Si ^a	164.0	67.4	76.6
Si ^b	167.5	65	80.1
Si ^c	159	61	85
HfO ₂ ^a	578.2	120.9	82.6
HfO ₂ ^d	477	113	100
ZrO ₂ ^a	513.9	122.7	72.3
ZrO ₂ ^d	508	132	78
ZrO ₂ ^e	409	53	60

^a Present work.

^b Experimental value at $T = 73$ K, see [23].

^c Calculated value through LDA and *ab initio* pseudopotentials, see [19].

^d Extrapolated to $Pp = 0$, according to Dole *et al* [24].

^e Calculated value through a theoretical empirical interatomic potential method [25].

bounds of elastic constants, respectively. Hill [21, 22], took an average of the two approaches and obtained a better agreement with experiments. We follow the last procedure and estimated the bulk modulus, shear modulus, Young’s modulus, Poisson’s coefficient and the longitudinal, transverse and mean elastic wave velocities for a given material, but in polycrystalline form.

The bulk modulus, for a cubic mono-crystal is defined as:

$$B_0 = \frac{1}{3}(C_{11} + 2C_{12}). \quad (5)$$

The shear modulus G_H is defined to be an average between of the shear moduli G_{Reuss} and G_{Voigt} [21]

$$\begin{aligned} G_H &= \frac{1}{2}[G_{\text{Reuss}} + G_{\text{Voigt}}] \\ 5G_{\text{Voigt}} &= C_{11} - C_{12} + 3C_{44} \\ \frac{5}{G_{\text{Reuss}}} &= 4(S_{11} - S_{12}) + 3S_{44} \end{aligned} \quad (6)$$

where S_{ij} are the compliance matrix elements and S is the inverse matrix of the elastic constants matrix C . For crystals with orthorhombic symmetry, the respective bulk modulus and shear modulus are:

$$\begin{aligned} B_H &= \frac{1}{2}(B_{\text{Reuss}} + B_{\text{Voigt}}) \\ B_{\text{Reuss}} &= [(S_{11} + S_{22} + S_{33}) + 2(S_{12} + S_{13} + S_{23})]^{-1} \\ B_{\text{Voigt}} &= \frac{1}{9}(C_{11} + C_{22} + C_{33}) + \frac{2}{9}(C_{12} + C_{13} + C_{23}) \\ G_H &= \frac{1}{2}(G_{\text{Reuss}} + G_{\text{Voigt}}) \\ G_{\text{Reuss}} &= 15[4(S_{11} + S_{22} + S_{33}) - 4(S_{12} + S_{13} + S_{23}) \\ &\quad + 3(S_{44} + S_{55} + S_{66})]^{-1} \\ G_{\text{Voigt}} &= \frac{1}{15}(C_{11} + C_{22} + C_{33} - C_{12} - C_{13} - C_{23}) \\ &\quad + \frac{1}{5}(C_{44} + C_{55} + C_{66}). \end{aligned} \quad (7)$$

From B_H and G_H , the Poisson coefficient (ν), Young's modulus (E) and the values for the speed of sound, longitudinal (v_l), transverse (v_t) and mean (v_m), are determined:

$$\begin{aligned} \nu &= \frac{\frac{1}{2}(B_H - \frac{2}{3}G_H)}{(B_H + \frac{1}{3}G_H)} \\ E &= \frac{9B_H}{(1 + \frac{3B_H}{G_H})} \\ v_t &= \sqrt{\frac{G_H}{\rho}} \\ v_l &= \left(\frac{(B_H + \frac{4}{3}G_H)}{\rho} \right) \\ v_m &= \left(\frac{1}{3} \left(\frac{2}{v_t^3} + \frac{1}{v_l^3} \right) \right)^{-\frac{1}{3}}. \end{aligned} \quad (8)$$

One of the standard methods of calculating the Debye temperature θ_D is from elastic constant data, since θ_D is proportional to the sound velocity (averaged) v_m by the equation [26]:

$$\theta_D = \frac{h}{k} \left[\frac{3q}{4\pi} \frac{N\rho}{M} \right]^{1/3} v_m \quad (9)$$

and where h/k have the usual meanings of quantum mechanics, N is Avogadro's number, ρ is the density, M is the molecular weight of the solid and q is the number of atoms in the molecule.

Experimental elastic constants B , E , G of unstabilized, partial and fully stabilized ZrO_2 and HfO_2 are porosity

dependent [1, 27, 28]. In order to compare with our theoretical assessments for a fluorite (cubic) structure, in which no porosity is included, one has to interpolate the available experimental elastic constant to null porosity. That should be possible to perform by, for example, using the following equations given by Dole *et al* [24] for unstabilized HfO_2 and the E , G and B data at a given porosity Pp :

$$\begin{aligned} E &= E_{(Pp=0)}e^{-4.17Pp} \text{ (GPa)} \\ G &= G_{(Pp=0)}e^{-3.93Pp} \text{ (GPa)} \\ B &= B_{(Pp=0)}e^{-5.48Pp} \text{ (GPa)}. \end{aligned} \quad (10)$$

The porosity comes from the appearance of vacancies and voids in the crystal. By adding to the solution atomic components different from Hf or Zr vacancies can be added. In order to stabilize the cubic and tetragonal phases, yttrium in the form of Y_2O_3 is added, where each mole of this compound adds a mole of oxygen vacancies. In the following paragraphs we describe how we model the effect of the added vacancies on elastic constants, using the equations (10) of Dole *et al* [28].

Data for $C_{11} = 380$ GPa, $C_{12} = 90$ GPa, $C_{44} = 80$ GPa [1, 29] are available for the alloy $\text{HfO}_2 - x\% \text{Y}_2\text{O}_3$, where $x = 12\%$. The formula $12\% \text{Y}_2\text{O}_3$ in the compound can be expressed as $\text{Y}_{0.24}\text{O}_{0.36}$. If there were no vacancies in the oxide, this formula should be written as $\text{Y}_{0.24}\text{O}_{0.48}$, thus the remaining term HfO_2 in the alloy should be $\text{Hf}_{0.76}\text{O}_{1.52}$. This yields as a result the stoichiometric formula $\text{Hf}_{0.76}\text{Y}_{0.24}\text{O}_{1.88}$, giving $(2-1.88)/3$ oxygen vacancies per atom in the matrix or 0.48 vacancies per 12-atom cell. The porosity hereby calculated is 0.0415%, defined as 0.48 times the percentage of the ratio of the O atom vacancy volume (0.796 au^3) and the 12-atom reference cell volume, in this case the cubic $Fm\bar{3}m$ with 9.73 au lattice constant. The calculated values for C_{11} , C_{12} and C_{44} for zero porosity in HfO_2 and assuming that each C_{ij} is related to the bulk modulus are:

$$\begin{aligned} C_{11} &= 380e^{5.48Pp} = 477 \text{ GPa} \\ C_{12} &= 90e^{5.48Pp} = 113 \text{ GPa} \\ C_{44} &= 80e^{5.48Pp} = 100 \text{ GPa}. \end{aligned} \quad (11)$$

Tables of elastic constants for $\text{ZrO}_2 - 12\% \text{Y}_2\text{O}_3$ (having the same 0.0415% porosity as the previous case) yield $C_{11} = 405.1$ GPa, $C_{12} = 105.3$ GPa and $C_{44} = 61.80$ GPa, thus the values at zero porosity are again 25.5% greater: $C_{11} = 508$ GPa, $C_{12} = 132$ GPa and $C_{44} = 78$ GPa. These values show good agreement with the hereby calculated values for ZrO_2 using FP-LMTO (see table 1). It must be taken into account that the volume used here for oxygen vacancies is approximate and was obtained from *ab initio* calculations with 12-atom cells and a oxygen vacancy.

Values are shown in table 2 for C_{11} , C_{22} , C_{33} , C_{12} , C_{13} , C_{23} , C_{44} , C_{55} and C_{66} for HfO_2 orthorhombic crystals, calculated through NFP-LMTO, and compared with those calculated through the empirical interatomic model potential (EMP) by Mirgorodsky *et al* [25]. The calculated values for C_{11} , C_{22} and C_{33} exceed 500 GPa, such as C_{11} in the $Fm\bar{3}m$ phase, while the group of stiffness constants for biaxial

Table 2. Elastic constants calculated for HfO₂ (*Pnma*), compared with theoretical and experimental values from the literature.

Constants (GPa)	NFP		PP-PW ^c		PP-PW ^d		PP-PW ^e	
	LMTO ^a	EMP ^b	LDA	LDA	GGA	LDA	GGA	
C_{11}	534	477	—	—	—	—	—	
C_{22}	556	415	—	—	—	—	—	
C_{33}	625	446	—	—	—	—	—	
C_{12}	194	172	—	—	—	—	—	
C_{13}	231	202	—	—	—	—	—	
C_{23}	236	151	—	—	—	—	—	
C_{44}	36	31	—	—	—	—	—	
C_{55}	106	117	—	—	—	—	—	
C_{66}	140	132	—	—	—	—	—	
B_0 (Th)	335	263	306	312	259	295	252	
B_0 (Exp)			332 ^f	340 ^g				

^a Present work.^b Reference [25].^c Reference [30].^d Reference [31].^e Reference [32].^f Experimental value, see [15].^g Experimental value, see [33].

deformations are of the order of 200 Pa, which is almost two times of that for C_{12} for the fluorite phase. This is a consequence of the higher density in *Pnma* HfO₂. Lastly, it is observed that there is a large anisotropy between the elastic rigidity constants C_{44} , C_{55} and C_{66} , which range from 36 to 140 GPa (see table 2)

This is also observed in the constants calculated with the EMP model, and this shows the strong anisotropy in the *Pnma* phase. It should be noted that the interatomic model potential is approximate; it is adjusted to reproduce the phonon frequencies and the effectiveness for predicting elastic properties is sometimes limited. For example (see table 1) $C_{11} = 409$ GPa in the EMP model compares well with experimental values for C_{11} of 417 GPa, although this is true for porous ZrO₂ (solid solution of ZrO₂ and Y₂O₃), which make doubtful the comparison with theoretical results without porosity. The bulk modulus calculated with such a model is 171 GPa, significantly below the value calculated with NFP-LMTO of 253 GPa. Nevertheless, it should be noted that we have made a very simple description of the dependence of the elastic constant on porosity, and no *ab initio* theoretical study of this sense is known to us.

The calculated elastic constants of *Pnma*-HfO₂ are shown in tables 2 and 3, compared with available data calculated with the EMP model. We found larger discrepancies with respect to this model in the stiffness constants C_{22} , C_{33} , corresponding to uniaxial strains along the *b* and *c* axes, and C_{23} corresponding to biaxial strains to the *b* and *c* axes as well. However, discrepancies for shear strains are not large. The average of the stiffness constants corresponding to uniaxial strains is about 550 GPa, which denotes a tough material. However, stiffness constants for biaxial strains are about 200 GPa, lower but anyway very high for an oxide. These six elastic constants give in turn a very high bulk modulus, $B = 335$ GPa. This is good in comparison with experimental data, $B = 332$ GPa [15] and

Table 3. Elastic and thermoacoustics properties in the polycrystal form.

Const./Comp.	<i>Fm3m</i>				<i>Pnma</i>	
	Si ^a	Si ^b	ZrO ₂ ^a	HfO ₂ ^a	HfO ₂ ^a	HfO ₂ ^c
B (GPa)	99.6	99.2	292.5	283.2	335	264
G (GPa)	63.7	66.9	141.9	130.5	108	94.6
E (GPa)	157.5	164.0	366.4	339.4	293	253.6
ν	0.236	0.224	0.291	0.300	0.354	0.34
v_l (m s ⁻¹)	5159.6	5361.2	4778.0	3484.3	2999	2806
v_t (m s ⁻¹)	8800.8	8993.5	8803.0	6521.4	6320	5698
v_m (m s ⁻¹)	5730.3	5934.5	5331.0	3892.0	3374	3150
θ_D (K)	633.0	650.6	786.1	576.3	471	440
B/G	1.56	1.48	2.06	2.17	3.1	2.79

^a Present work.^b Obtained values by means of experimental elastic constants, see [23].^c Calculated with data taken from the EMP model [25].

$B = 340$ GPa [33]. Our previous theoretical LDA calculations utilizing the SIESTA code, *ab initio* pseudopotentials (which includes Hf partial core corrections) and the double-zeta local basis set gave 328 GPa. Other LDA *ab initio* assessments gave $B = 306$ GPa [30], $B = 312$ GPa [31] and $B = 295$ [32]. The last authors reported, utilizing the GGA approach, even lower values: $B = 259$ GPa [31] and $B = 252$ GPa [32]. These important underestimations certainly proscribe the utilization of GGA in the calculation of accurate elastic constant in these oxides. Therefore, it seems that the present all-electron LDA model accounts well for bond stretching interatomic forces. In the case of shear moduli, we found similar values to the EMP model, with large anisotropy between sliding planes with shear strains of u_4 and u_5 and u_6 . The shear efforts to deform the crystal along *yz* planes are much lower than the *xz* and *xy* planes, respectively. This also affects the polycrystal shear stiffness constant G , which drops from 130.5 GPa in the *Fm3m* phase to 108 GPa in the *Pnma* phase. However, it is higher than the value of 96 GPa calculated for the EMP model. This fact also enhances the B/G value, which increases to 3.1, and the Poisson constant to 0.345, denoting more ductile than brittle behavior in this calculation. Since G measures the resistance to plastic deformations, if we look at a material with higher strength it is preferable the utilization of the *Fm3m* phase, which has lower bulk modulus (more compressible) but higher G constants. We have to comment that this phase is the stable one for un-doped particles with nano-grain sizes of less than 2 nm.

4. Conclusions

An *ab initio* determination was made of the elastic coefficients for cubic phase ZrO₂ and HfO₂ in cubic and orthorhombic phases, and, from these, the mechanical and thermo-acoustic properties of the same polycrystals. These compounds, which possess high bulk moduli, turn out to be very hard materials and are predicted to be show more ductility than brittleness. These properties of high hardness and ductility suggest that these materials are important for the optics and metallurgical industries. The estimated elastic constants C_{ij} are shown to

have good agreement with experimental values extrapolated to zero porosity in the cubic phase of ZrO₂, although for HfO₂ in the same phase there is a discrepancy in C_{11} that should be investigated, with more experimental approaches being particularly called for. The values for the elastic constants for orthorhombic HfO₂ have been compared to those calculated by the EMP model, while the bulk moduli obtained are in excellent agreement with experimental values. However, we have to wait for new elastic constant measurements to compare with our predictions. Finally, we found that in the case of an all-electron calculation like the present one, the semicore 4f¹⁴ electrons need to be included in the valence to get reliable two-body interatomic forces and therefore accurate elastic properties. In the case of pseudopotential calculations it seems that this is taken into account with the inclusion, in Hf atomic pseudopotentials, of partial core corrections [16].

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