Gazi University Journal of Science
GU J Sci
27(1):627-636 (2014)

First principles LDA+U and GGA+U study of HfO_2: Dependence on the effective U parameter

Yasemin Ö. ÇİFTCİ[1,♠], A.H. ERGÜN[1], K. ÇOLAKOĞLU[1], E. DELİGÖZ[2]

[1]*Gazi University, Department of Physics, Teknikokullar, 06500, Ankara, TURKEY*

[2]*Aksaray University, Department of Physics, 68100, Aksaray, TURKEY*

Received: 23.08.2013 Revised: 29.09.2013 Accepted: 29.12.2013

ABSTRACT

We have performed first-principles calculations of the structural, electronic, mechanical, and vibrational properties of HfO_2 based on the density functional theory with Local Density Approximation (LDA), Generalized Gradient Approximation(GGA), the LDA + U and GGA+U approaches based on the density functional theory (DFT). In orderd to describe precisely the strong on-site Coulomb repulsion among the localized Hf 5d electrons, we adopt the LDA+U and GGA+U formalism for the exchange correlation term. For the total-energy calculation we have used the projected augmented plane-wave (PAW) implementation of the Vienna Ab initio Simulation Package (VASP). The dependence of selected properties of this material on the effective U parameter has been investigated in detail. We have used to examine structure parameter in Fluorite(C1) structure of HfO2. The equilibrium geometries, the total and partial densities of states, elastic constants, elastic moduli, Poisson's ratio, Zener anisotropy factor, Young's modulus and shear modulus and phonon dispersion curves for this material are systematically investigated and analyzed in comparison with experiments and previous calculations. We show for the first time that the addition of an on-site Hubbard repulsion term to the LDA and GGA leads to improved agreement between calculated and experimental values of structural and electronic properties, except for elastic properties.

Key Words: *Hafnia, LDA+U, GGA+U, First-principles calculation, mechanical properties, electronic structure, phonon dispersion.*

[♠] Corresponding author, e-mail: yasemin@gazi.edu.tr

1. INTRODUCTION

Hafnium-based oxides have been extensively investigated by experiments [1–3] and theoretical calculations [4–6]. HfO_2 has attracted much more attention because of its excellent dielectric properties, wide band gap, high bulk modulus, high melting point, etc. [7,8]. Hafnium oxides (Hafnia) applications include the use in catalysis, paints additives, oxygen sensors, fuel cells, as a thermal barrier coating in engines and gate-dielectric materials in metal-oxide-semiconductor (MOS) devices [9–12] and transistors in the microchipes. In particular, HfO_2 exists in three polymorphs at atmospheric pressure. Under low temperature, the bulk HfO_2 has monoclinic symmetry (C_5^{2h} or $P2_1/c$), and its phase transforms to tetragonal phase (D_{4h}^{15} or $P4_2/$ nmc) and cubic phase (O^5_hor Fm3m) at around 2000 and above 2870 K, which in turn melts at 3118K [4,13].

The electronic and structural properties of HfO_2 have been extensively studied before in detail within ab initio total energy calculations [14–25]. Caravaca and Casali [26] calculated the electronic, elastic and equilibrium properties of HfO_2 using the SIESTA program packet based on pseudopotentials and a localized basis set. Terki et al. [5] investigated the structural, elastic and electronic properties of cubic HfO_2 using the full potential linearized augmented plane-wave method (FP-LAPW) based on the WIEN2k code. Zhao and Vanderbilt [4] calculated the structural, vibrational and lattice dielectric properties of HfO_2 using both localized density approximation (LDA) and generalized gradient approximation (GGA). Rignanese et al. [27] have studied the Born effective charge tensors, the phonon frequencies and the dielectric permittivity tensors of cubic and tetragonal phases of HfO_2 using LDA performed using the ABINIT package. Atashi et al. [28] have calculated the structural and electronic properties of HfO_2 surfaces using the VASP. Liu et al. [29] have investigated the relations between electronic structure and optical properties using the theory about crystal-field and molecular-orbital bonding using the CASTEP code. Recently, Liu et al. [30] have investigated electronic structure, effective masses, mechanical and thermo-acoustic properties of cubic HfO_2 under pressure. The same authors [31] have also studied structural, elastic and electronic properties of tetrogonal HfO_2 under pressures. The structural, elastic and thermodynamic properties of cotunnite-type phase of Hafnia under high pressure from first-principles calculations have been reported by Zhu et al. [32].

Conventional density functional theory (DFT) that apply the local density approximation (LDA) or generalized gradient approximation (GGA) underestimates the strong on-site Coulomb repulsion of the 4d electrons and, consequently, describes HfO_2 incorrect. One more promising way to improve the drawback is LDA+U or GGA+U approach, in which the underestimation of the strong in- triatomic Coulomb interaction is corrected by the Hubbard U parameter.

However, to our knowledge, a systematical theoretical investigation of electronic structure, mechanical and vibrational properties for HfO_2 is still lacking. Consequently, based on the good performance of LDA/GGA+U approaches in describing the electronic structure of the strong-correlation systems, we carried out the present study of HfO_2.

In this present study, we use the LDA + *U* and GGA + *U* schemes due to Dudarev et al. [33] to investigate the lattice parameter, electronic structure, elastic constants, Poisson’s ratio, and phonon dispersion of HfO_2. We discuss how these properties are affected by the choice of U as well as the choice of exchange-correlation potential, i.e, the LDA or the GGA. Our results show that the pure LDA or GGA fails to give the accurate lattice parameter and correct electronic structure, while the LDA+U and GGA+U schemes can effectively remedy these failures.

The paper is organized in the following way. The details of our calculations are described in Section 2 and in Section 3 we present and discuss the results. In Section4, we summarize our findings.

2. METHOD AND CALCULATION

Density-functional theory calculations are performed with the density functional theory (DFT) and the Vienna ab initio simulation package (VASP) [34] using the local density approximation (LDA) and generalized gradient approximation (GGA) for the exchange correlation potential [35,36]. The projected augmented wave (PAW) method of Blöchl [37] is implemented in VASP with the frozen-core approximation. It is well-known that the input parameters in these calculations are only the atomic number and atomic positions in the unit cell of considered material. For the plane-wave set, a cutoff energy of 500 eV is used. The *k*-point meshes in the full wedge of the Brillouin zone (BZ) are sampled by 10x10x10 grids according to the Monkhorst-Pack[38]. The hafnium $5p^6 6s^1 5d^3$ and oxygen $2s^2 2p^4$ electrons are treated as valence electrons. The strong on-site Coulomb repulsion among the localized Hf 5*d* electrons is described by using the formalism developed by Dudarev et al. [33]. In this scheme, the total LDA (GGA) energy functional is of the form

$$E_{LDA(GGA)+U} = E_{LDA(GGA)} + \frac{U-J}{2}\sum_{\sigma}[Tr\rho^{\sigma} - Tr(\rho^{\sigma}\rho^{\sigma})] \qquad (1)$$

where ρ^{σ} is the density matrix of d states, and *U* and *J* are the spherically averaged screened Coulomb energy and the exchange energy, respectively. In this work, the Coulomb U is treated as one variable, while the parameter J is set to 1 eV. Since only the difference between U and J is meaningful in Dudarev’s approach, therefore, we label them as one single parameter U for simplicity.

3. RESULTS AND DISCUSSION

3.1. Structural and Electronic Properties

HfO_2 is an insulator featuring cubic *Fm3m s*tructure of CaF_2 with experimentally determined lattice parameter a_o=5.08 A [39]. The present calculated lattice parameter ao, bulk modulus (B) and pressure derivatives of bulk modulus (B’) were obtained by minimizing the corresponding energy at constant volumes and by fitting a Murnaghan equation [40]. The calculated energy-volume data for series of values of U within the LDA and GGA schemes are shown in Fig.1 and Fig.2, respectively. After the fitting of the data in Fig.1 and Fig.2 by Murnaghan equation of state, the derived lattice parameter a_o and bulk modulus B as a function of *U* are shown in Fig.3 and 4, respectively.

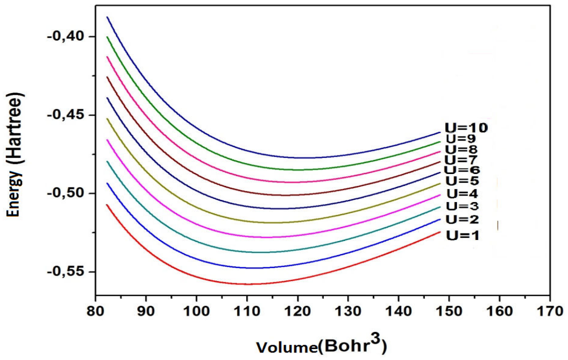


Figure 1. Energy versus volume curves for different LDA+U schemes of HfO$_2$ compound.

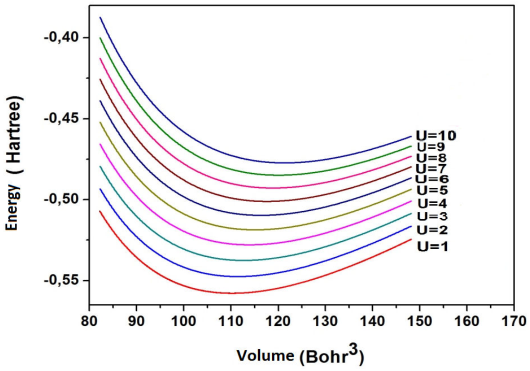


Figure 2. Energy versus volume curves for different GGA+U schemes of HfO$_2$ compound.

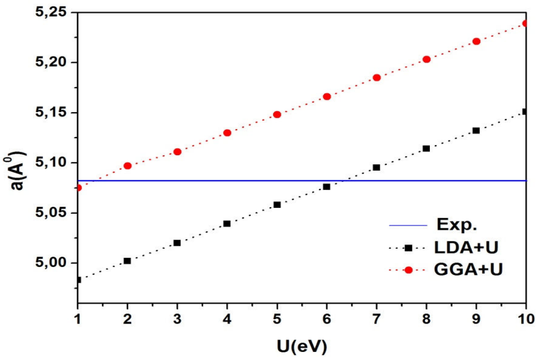


Figure 3. Lattice parameters versus Hubbard U for HfO$_2$ with experimental data.

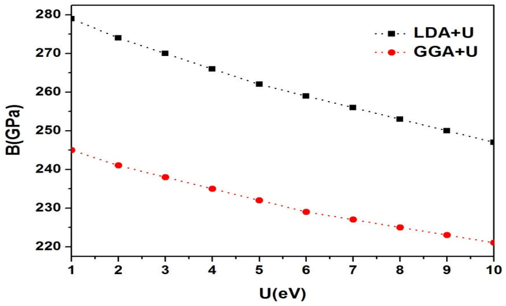


Figure 4. Bulk modulus versus Hubbard U for HfO$_2$ compound.

The calculated results as a function of U within the LDA+U and GGA+U schemes are collected in Table1 and 2, respectively. In order to make a comparison, the experimental lattice constant is also listed. It can be seen from Fig.3 that the relation between ao and *U* does not follow a simple monotonically linear function for both the LDA and GGA. At small values of *U* (<1eV), the change in lattice parameter is somewhat insensitive to the variation of *U,* and both the LDA and the GGA underestimate the lattice parameter for *U*=0 eV. This feature rarely occurs in the usual DFT calculations. In most cases, the LDA generally underestimate the lattice parameter while the GGA genarally overestimate. When *U* is increased to 1eV, then a_o starts to rapidly go up with *U*. The experimental values of ao=5.08A is well fitted at U=6eV and 1eV for the LDA and GGA, respectively. It can be seen from Fig.4 that the calculated bulk modulus B varies with over a rather broad range from 247 to 279GPa for the LDA and from 221 to 245 GPa for the GGA. In particular, the LDA at U=6eV gives a bulk modulus B=259 GPa while the GGA at U=1eV gives B= 245GPa . At present there are no experimental data of bulk modulus available for HfO$_2$.The bulk modulus B calculated by the LDA is always higher than the GGA results, this is because the LDA approach overbinds the compounds.

Table 1. Calculated equilibrium lattice parameter (*a*), bulk modulus (B), and its pressure derivative (B') for HfO_2 **by the LDA+U scheme.**

LDA	Ref.	U=0	U=1	U=2	U=3	U=4	U=5	U=6	U=7	U=8	U=9	U=10
a	5,07[a] 5,11[b]	4,984	4,984	5,002	5,020	5,039	5,058	5,076	5,095	5,114	5,132	5,151
B	289[c]	279	279	274	270	266	262	259	256	253	250	247
B'	-	4,162	4,163	4,093	4,026	3,962	3,900	3,842	3,786	3,732	3,681	3,632

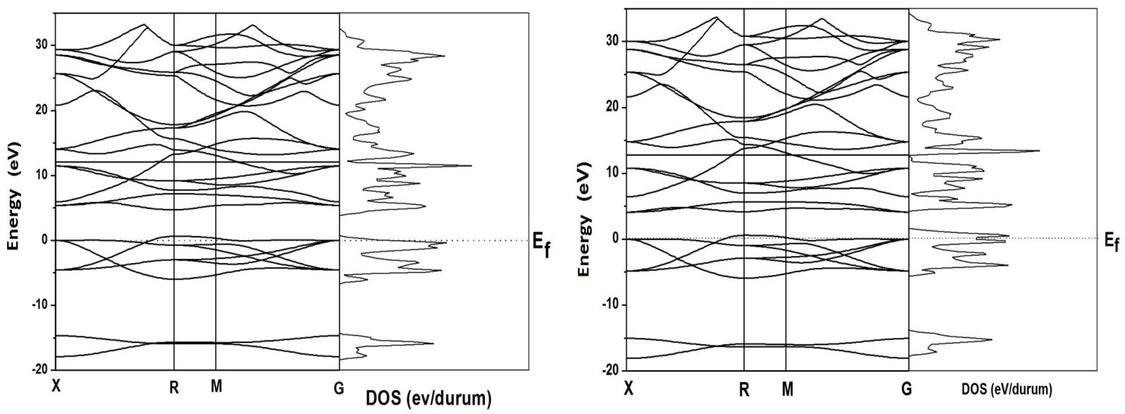
a:[29], b:[42], c:[43]

Table 2. Calculated equilibrium lattice parameter (*a*), bulk modulus (B), and its pressure derivative (B') for HfO_2 **by the GGA+U scheme.**

GGA	Ref.	U=0	U=1	U=2	U=3	U=4	U=5	U=6	U=7	U=8	U=9	U=10
a	5,07[a] 5.09[b]	5,074	5,075	5,097	5,111	5,130	5,148	5,166	5,185	5,203	5,221	5,239
B	257[c]	245	245	241	238	235	232	229	227	225	223	221
B'	-	4,199	4,196	4,129	4,064	4,003	3,946	3,891	3,840	3,790	3,745	3,699

a:[29], b:[13], c:[43]

Besides the above effect of the LDA+U and the GGA+U on the atomic-structure parameters, in the following, we further systematically investigate how the LDA+U and GGA+U schemes affect the electronic structure. The structural feautures in Fig.3 and 4 are closely related the electronic structure of HfO_2. From the above results and discussion, we conclude that the U= 6 and 1eV gives more accurate lattice parameter for the LDA+U and GGA+U approachs, respectively. Therefore, we have calculated the band structure using the above scheme in the following. The calculated band structures for HfO_2 along the high symmetry directions in the first Brillouin zone are shown inFig. 5(a) and(b) for LDA+U and GGA+U approachs, respectively. Here in some of the earlier DFT calculations, band gap values have given as 2,8eV in [41] and 3,4eV in [42] and the experimental value is 5,7eV [43].



(a)

(b)

Figure 5. (a) Calculated band structures and corresponding DOS for LDA+U approach.
(b) Calculated band structures and corresponding DOS for GGA+U approach.

The total DOS for HfO_2 and the projected DOSs for Hf 5p and O 2s orbitals calculated within the LDA+U and the GGA+U approaches are shown in Fig. 6 (a) and (b), respectively. Fermi energy has been set to be zero. It can be seen from Fig.6 that the lowest valence state is essentially dominated by Hf 5p electrons. When U parameter increases, we found that DOS curves exhibit same features. The biggest peak in the valance region increase with U parameters. In regions near Fermi level, as *U* increases, the peaks in the valence states shift to the lower energies, and the peaks in the conduction states shift to the higher energies, and then, the gap increases with the U parameter. Fig.7 displays band gap energy as a function of U for the LDA+U and the GGA+U approaches. When U >1 eV, the band gap values increase with U increasing. But for both the LDA+U and the GGA+U approaches, the calculated band gap values are still underestimated by compared with the experimental value.

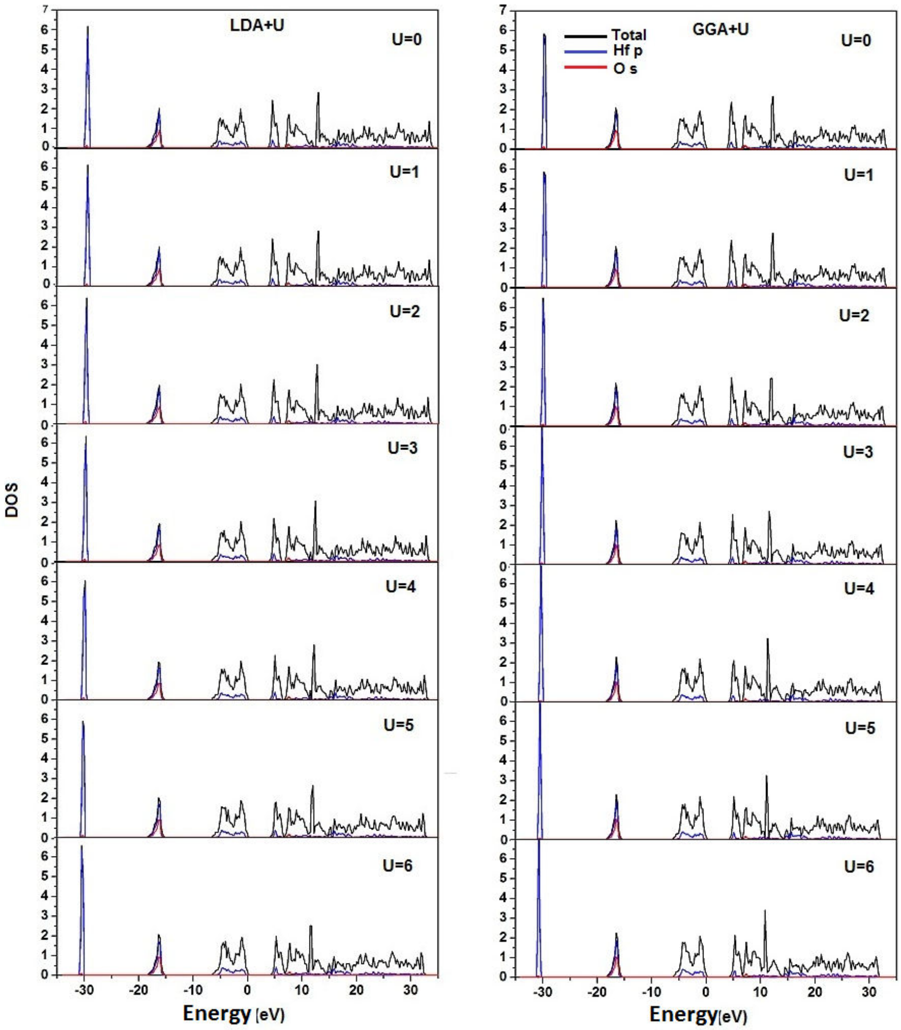


Figure 6. Partial DOS case for both LDA+U and GGA+U approaches of HfO_2.

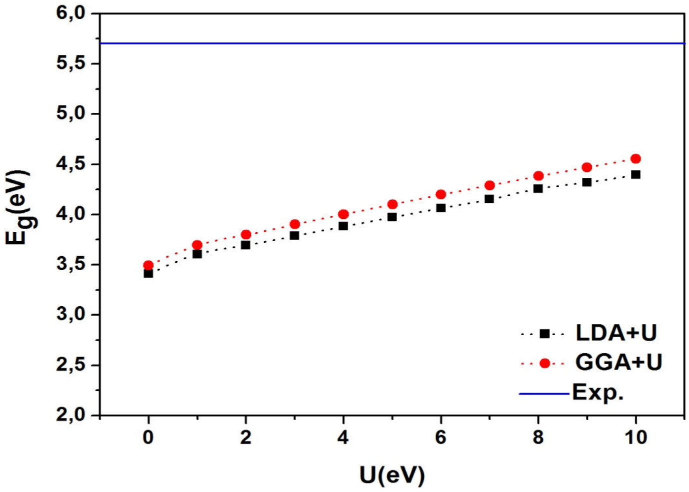


Figure 7. Band gap versus Hubbard U with experimental data for HfO_2 compound.

3.2. Elastic Properties

Elastic constants are very important properties of solids because their information usually contains the interatomic interaction potentials, the fundamental properties of the solid state. A study of the elastic properties for materials is essential to understand the chemical bonding and the cohesion of material [44]. In this study, the second-order elastic constants (C_{ij}) are calculated using the "stress-strain" relations [45]. The calculated results of elastic constants of HfO_2 using the LDA+*U* and GGA+*U* schemes are collected in Tables 3 and 4. The traditional conditions for mechanical stability of cubic crystals are: C_{11}-C_{12} >0, C_{11}>0, C_{44} >0, $C_{11}+2C_{12}$ >0, $C_{12} < B < C_{11}$. Our calculated elastic constants satisfy these stability conditions for both approaches of HfO_2. Therefore, fluorite (C1) structure of HfO_2 is mechanically stable. For the results calculated by LDA + U and GGA + U approaches, one can see that the calculated elastic constant C_{11} is larger than the experimental value of 477 GPa. For both approaches, C_{11} increases first and then decreases with increasing the Hubbard U parameter. As for C_{12}, at a typical value U = 6 eV, the LDA + U gives C_{12} = 113,65 GPa, which is in excellent agreement with the experimental values. Note that the GGA + U result of C_{12} and C_{44} is smaller than the experimental values of 113GPa and 100 GPa, on the other hand LDA + U result of the same constant is larger than the experimental value. Generally speaking, the obtained results clearly show that the the effect of the Hubbard term is insignificant for mechanical properties and support the results of earlier reports[46].

Table 3. Calculated and experimental elastic constants (GPa) for HfO2 by the LDA+U scheme.

	U	C_{11}	C_{12}	C_{44}
HfO_2	**Exp.^{a}**	**477**	**113**	**100**
	0	628,84	118,10	111,80
	1	632,61	123,56	119,18
	2	621,33	121,05	119,61
	3	610,25	119,11	119,06
	4	598,47	116,36	118,64
	5	588,62	115,57	118,29
	6	578,56	113,65	118,15
	7	568,27	111,57	117,08
	8	559,94	110,52	116,24
	9	549,39	108,75	114,98
	10	539,78	107,55	115,16

Table 4. Calculated and experimental elastic constants (GPa) for HfO_2 by the GGA+U scheme.

	U	C_{11}	C_{12}	C_{44}
HfO_2	**Exp.**[a]	**477**	**113**	**100**
	0	568,86	94,64	89,05
	1	572,34	99,44	95,37
	2	563,12	97,81	95,56
	3	555,38	96,41	95,75
	4	545,51	94,74	95,13
	5	536,40	93,51	94,97
	6	528,72	92,18	95,55
	7	521,17	91,17	95,02
	8	514,57	90,98	95,06
	9	506,69	90,88	96,12
	10	499,98	90,41	96,31

The elastic properties such as the Zener anisotropy factor (A), Poisson's ratio (v), Young's modulus (E) are often measured for polycrystalline materials. The Zener anisotropy factor A is calculated using the relation [43]: $A = 2C_{44}/(C_{11} - C_{12})$. Poisson's ratio, and Young's modulus E are calculated in terms of computed data by using the following relations [47]:

$$v = \frac{3B-2G}{2(3B+G)} \tag{2}$$

And

$$E = 9GB/(G + 3B) \tag{3}$$

where $G = (G_V + G_R)/2$ is the isotropic shear modulus. G_V is Voigt's shear modulus corresponding to the upper bound of shear modulus (G), while G_R is Reuss's shear modulus corresponding to the lower bound of shear modulus. For cubic crystals, G_V and G_R can be written as $G_V = (C_{11} - C_{12} + 3C_{44})/5$, and $5/G_R - 4/(C_{11} - C_{12}) + 3/C_{44}$.

Calculated Zener anisotropy factor, Poisson's ratio, Young's modulus, shear modulus C' for HfO_2 within LDA+U and GGA+U approachs are also given in Table 5 and 6, respectively. Moreover, the bulk modulus is a measure of resistance to volume change by applied pressure, whereas the shear modulus is a measure of resistance to reversible deformations upon the shear stress [48]. And, Young modulus E (the ratio between stress and strain) is required to provide information about the measure of the stiffness of the solids.

Zener anisotropy factor A is a measure of the degree of elastic anisotropy in solids. The A takes the value of 1 for a completely isotropic material. If the value of A smaller or greater than unity it shows the degree of elastic anisotropy. The calculated Zener anisotropy factors for HfO_2 are equal to 0.437 and 0.375 for U=0 in the LDA+U and the GGA+U approaches, which indicates that this compound is anisotropic. Additionally, the Poisson's ratio is very important property for industrial applications since provides more information about the characteristics of the bonding forces than the elastic constants. The lower limit and upper limit of v are given 0.25 and 0.50 for central forces solids, respectively [49]. Calculated v values are equal to 0.263 and 0.269 for for U=0 in the LDA+U and the GGA+U approaches. It is concluded that the interatomic forces in the HfO_2 are central.

Table 5. Calculated Zener anisotropy factor (*A)*, Poisson's ratio (ν), Young's modulus (E), shear modulus (C') by the LDA+U scheme.

	U(eV)	C'[GPa]	E[GPa]	Y	A
HfO_2	0	156,732	396,048	0,2634562	0,4377961
	1	162,349	407,941	0,2563661	0,4682356
	2	161,492	404,538	0,2525030	0,4781722
	3	159,813	400,456	0,2528881	0,4848312
	4	158,244	396,188	0,2518257	0,4921699
	5	156,718	392,082	0,2509097	0,5001163
	6	155,475	388,630	0,2498109	0,5082704
	7	153,505	383,732	0,2499024	0,5127330
	8	151,841	379,540	0,2497941	0,5172890
	9	149,642	374,300	0,2506443	0,5218773
	10	147,827	369,913	0,2511636	0,5282373

Table 6. Calculated Zener anisotropy factor (*A)*, Poisson's ratio (ν), Young's modulus (E), shear modulus (C') by the GGA+U scheme.

	U(eV)	C'[GPa]	E[GPa]	Y	A
HfO_2	0	133,485	338,917	0,2694882	0,3755641
	1	138,534	349,703	0,2621548	0,4033411
	2	137,714	347,155	0,2604202	0,4107369
	3	137,049	344,986	0,2586230	0,4172386
	4	135,482	341,671	0,2609491	0,4220778
	5	134,325	337,857	0,2576109	0,4288650
	6	133,955	336,495	0,2558597	0,4377606
	7	132,668	333,150	0,2555720	0,4419535
	8	131,849	330,919	0,2549146	0,4488302
	9	131,645	329,998	0,2533621	0,4623265
	10	130,939	328,063	0,2527348	0,4704015

It is shown from Table 5 and 6 that the mechanical properties such as, shear modulus, Poisson's ratio and Young modulus increase up to U=1eV with U increasing. After U=1eV, Poisson's, shear modulus and Young modulus decrease with U. Zener anisotropy factor increase in the whole range of U .

3.4. Phonon Dispersion Curves

The present phonon frequencies of HfO_2 compound in fluorite structure are calculated using the PHON code [50] and the related forces are obtained by the VASP package. The PHON code calculates force constant matrices and phonon frequencies using the "small displacement method" as described in Refs. [50, 51]. Phonon dispersion curves for HfO_2 have calculated within LDA+U formalism with $U = 6$ eV. For the phonon dispersion calculation, we use the 2×2×2 supercell containing 48 atoms and the 10×10×10 Monkhorst–Pack *k*-point mesh for the Brillouin zone integration. In order to calculate the Hellmann-Feynman forces, we displace four atoms two Hf and two O atoms from their equilibrium positions and the amplitude of all the displacements is 0.04 Å. Since there are three atoms in the primitive cell, there are three acoustic modes and six optical modes. The calculated phonon dispersion curves along the *Γ-X-Γ-L-X-W* directions are displayed in Fig.8. There are no experimental data and theoretical results on the lattice dynamics of this compound in literature for comparison with the present ones.

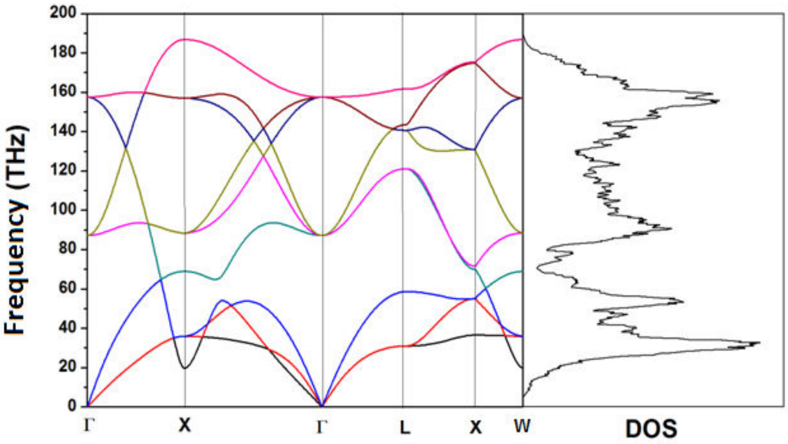


Figure 8. Phonon dispersion curves and phonon density of sates for LDA+U approach.

4. SUMMARY AND CONCLUSION

In summary, we have investigated the structural, electronic, mechanical and vibrational properties of HfO_2 within the LDA+U and GGA+U frameworks. The atomic structure, including the lattice parameters and bulk modulus, and the mechanical elastic properties have been systematically investigated as a function of the effective on-site Coulomb repulsion parameter U. From the study of the lattice parameter of HfO_2 we find that the experimental data of a_o can be well fitted by the LDA using U=6 eV, while by the GGA using U=1eV. It has also been shown in this study that the incorrect ground state at pure LDA or GGA (U=0) for HfO_2 can be readily corrected by the systematic inclusion of non-zero U. The other mechanical data such as Zener anisotropy factor (A), Poisson's ratio (v), Young's modulus (E), shear modulus (C') are determined for the first time. The results of mechanical elastic constants and phonon dispersion curves are also considered to be reasonable although some discrepancies exist. We have concluded that the computational results for HfO_2 are very sensitive of functional (LDA, GGA) and treatment of correlation effects (U value) for structural and electronic properties except for mechanical properties.

REFERENCES

[1] He, G., Zhu, L.Q., Liu, M., Fang, Q., Zhang, L.D., ***Appl. Surf. Sci.,*** 253, 3413(2007).

[2] Aarik, J., Ma¨ndar, H., Kirm, M., Pung, L., ***Thin Solid Films,*** 466, 41, (2004).

[3] Renault, O., Rarrett, N.T., Samour, D., Quiais-Marthon, S., ***Surf. Sci.,*** 526: 566–568 (2004).

[4] Zhao, X.Y., Vanderbilt, D., ***Phys. Rev. B,*** 65: 233106(2002).

[5] Terki, R., Feraoun, H., Bertrand, G., Aourag, H., ***Comput. Mater. Sci***., 33: 44(2005).

[6] Cockayne, E., ***Phys. Rev. B*** 75, 094103 (2007).

[7] Weir, B.E., Silverman, P.J., . Alam, M.A, Baumann, F., Monroe, D., Ghetti, A., Bude, J.D., Timp, G.L., Hamad, A., Oberdick, T.M., Zhao, N.X., Ma, Y., Brown, M.M., Hwang, D., Sorsch, T.W., ***IEDM Tech. Dig***., 437 (1999).

[8] Cao, M., Vande Voorde, P., Cox, M, Greene, W., ***IEEE Electron Device Lett***., 19: 291 (1998).

[9] Fleming, W.J., ***J. Electrochem. Soc.,*** 21: 124(1977).

[10] Alcock, C.B., ***Mater. Sci. Res***., 419:10 (1975).

[11] Waldorf, A.J., Dobrowolsk, J.A.I, Sullivan, B.T., Plante, L.M., ***Appl. Opt***., 5583: 32(1993).

[12] Wilk, G.D., Wallace, R.M., Anthony, J.M., ***J. Appl. Phys***., 5243: 89(2001).

[13] Terki, R., Bertrand, G., Aourag, H., Coddet, C., ***Mater. Lett***. ,62: 1484 (2008).

[14] Boyer, L.L., Klein, B.M., ***J. Am. Ceram. Soc.,*** 278 : 68 (1985).

[15] Cohen, R.E., Mehl, M.J., Boyer, L.L., ***Physica B*** 1, 150 (1988).

[16] Jansen, H.J.F., Gardner, J.A., ***Physica B***, 10: 150 (1988).

[17] Jansen, H.J.F., ***Phys. Rev. B***, 7267, 43(1991).

[18] Jomard, G., Petit, Pasturel, T. A., Magaud, L., Kresse, G., Hafner, J., ***Phys. Rev. B***, 4044 59 (1999).

[19] Stapper, G., Bernasconi, M., Nicoloso, N., Parrinello, M**., *Phys. Rev. B***,797, 59(1999).

[20] Fabris, S., Paxton, A.T., Finnis, M.W., ***Phys. Rev. B*** 6617, 61(2000).

[21] Foster, A.S., Sulimov, V.B., Lopez Gejo, F., Shluger, A.L., Nieminen, R.M., ***Phys. Rev. B*** 224108-1, 64 (2001).

[22] Dabrowski, J., Zavodinsky, V., Fleszar, A**., *Microelectron. Reliab***. 1093, 41(2001).

[23] Foster, A.S., Shluger, A.l., Nieminen, R.M**., *Phys. Rev. Lett.,*** 225901-1, 89 (2002).

[24] Lin, W., Kang, J., Zhu, Z., ***Mater. Sci. Eng. B,*** 553: 99(2003).

[25] Foster, A.S., Lopez Gejo, F., Shluger, A.L., Nieminen, R.M., ***Phys. Rev. B*,** 174117-1, 65 (2002).

[26] Caravaca, M.A., Casali, R.A., ***J. Phys.: Condens. Matter*,** 17: 5795 (2005).

[27] Rignanese, G.M., Gonze, X., Jun, G, Cho, K., Pasquarello, A., **Phys. Rev. B,** 69:184301 (2004).

[28] Atashi, B.M., Javier, F.S., Charles, B.M., ***Phys. Rev. B,*** 73: 115330(2006).

[29] Patil, S.K.R., Wang, Y.X., ***Phys. Stat. Sol. B***, 247: 54 (2010).

[30] Liu, Q. et al., ***Physica B*,** 404: 3614–3619 (2009).

[31] Liu, Q.J., Liu, Z.T., Feng, L., Xu, B., ***Physica Stat. Solidi B***, 248: 4950 (2011).

[32] Liu, Q.J., Liu, Z.T., Feng, L., ***Commun. Theor. Phys.*,** 56: 779(2011).

[33] Zhu, J.B., Ren, H.S., Zhu, J., Hao, Y. J., Liu, J., Zhang, C. M., Long, X.J., ***Physica B***, 406: 2501, (2011).

[34] Dudarev, S.L., Botton, G.A., Savrasov, S.Y., Humphreys, C.J., Sutton, A.P., ***Phys. Rev.B,*** 57: 1505(1998).

[35] Kresse, G., Hafner, J., ***Phys. Rev. B,*** 48 : 13115(1993).

[36] Kohn, W., Sham, L.J., ***Phys. Rev***., 140, A1133(1965).

[37] Wang, Y., Perdew, J.P., ***Phys. Rev. B,*** 44: 13298 (1991).

[38] Bl¨ochl, P. E., ***Phys. Rev. B*** , 50: 17953 (1994).

[39] Monkhorst, H. J., Pack, J.D., ***Phys. Rev. B,*** 13: 5188 (1976).

[40] Stacy, D.W., Johnstone, J.K., Wilder ,D.R**., *J. Am. Ceram. Soc***., 55 (1972).

[41] Murnaghan, F. D., ***Proc. Natl., Acad. Sci***., USA : 30, 5390 (1994)

[42] Demkov, A.A., ***Phys.Stat.Sol. B***, 226, No.1 (2001)

[43] Wang, J., Li, H.P., Stevens, R., ***J. Of Mat. Sci***., 27: 5397(1992)

[44] He, G. et al., ***Appl. Surf. Sci***., 253 (2007)

[45] Medvedeva, N.I., Zhukovi, V.P., Khodos, M.Y., Gubanov, V.A., ***Phys. Status. Sol.***, 160: 517 (1990)

[46] Nielson, O. H., Martin, R.M., ***Phys. Rev. Lett***., 50, 697 (1983).

[47] Mayer, V.B., Anton, H., Bott, E., Methfessel, M., Sticht, J., Haris, J., Schmidt, P. C., ***Intermetallics*** 11, 23 (2003).

[48] Sevik, C., Çağın, T., ***Phys. Rev. B***, 80, 014108(2009)

[49] Young, A. F., Sanloup, C., Gregoryanz, E., Scandolo, S., Hemley, R. E., Mao, H. K., ***Phys. Rev. Lett.,***96: 155501(2006).

[50] Watt, J.P., Peselnick, L., ***J.App. Phys***., 51: 1525 (1980).

[51] http://chianti.geol.ucl.ac.uk/~dario/ (1998).

[52] Alfè, D., Price, G. D., Gillan, M. J., ***Phys. Rev. B***: 64, 045123 (2001).

[53] Kresse, G., Furthmüller, J. and Hafner, J., ***Europhys. Lett.,*** 32: 729 (1995).