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Novel compounds in the Zr–O system, their crystal structures and mechanical properties

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With the motivation of exploring new high-strength ceramics, *ab initio* evolutionary simulations are performed to search for all the stable compounds in the Zr–O system. We have found that not only the traditional compound ZrO_2, but also the ordered suboxides $R\bar{3}$-Zr_6O, $R\bar{3}c$-Zr_3O, $P\bar{3}1m$-Zr_2O and $P\bar{6}2m$-ZrO are stable at zero pressure. The crystal structure of semimetallic $P\bar{6}2m$-ZrO consists of Zr-graphene layers and can be described as an intercalated version of the ω-Zr structure. An interesting massive Dirac cone is found in the three-dimensional (3D) band structure of $P\bar{6}2m$-ZrO at the Γ-point. The elastic properties, the hardness and the correlation between the mechanical properties of Zr–O compounds and the oxygen content have been systematically investigated. Surprisingly, the hardest zirconium oxide is not ZrO_2, but ZrO. Both $P\bar{6}2m$-ZrO and $P\bar{3}1m$-Zr_2O exhibit relatively high hardness values of 14 GPa and 10 GPa, respectively. The anisotropic Young's modulus E, torsion shear modulus G_t and linear compressibility β have been derived for $P\bar{6}2m$-ZrO and $P\bar{3}1m$-Zr_2O. Further analyses of the density of states, the band structure and the crystal orbital Hamilton population indicate that the electronic structure of Zr–O compounds is directly related to their mechanical properties. The simultaneous occurrence of the 3D-framework of Zr–O and the strong Zr–Zr bonds in $P\bar{6}2m$-ZrO explains its high hardness.

I. Introduction

Zirconia (ZrO_2) is an important modern ceramic material. It can be used as a refractory material, a high-κ dielectric constant material, a component in structural ceramics, a substitute for diamond and as an optical material.[1,2] Under ambient conditions, it is well known that ZrO_2 has a monoclinic $P2_1/c$ baddeleyite structure, which then transforms into orthorhombic-I (*Pbca*, OI) and orthorhombic-II (*Pnma*, OII) phases upon increasing pressure.[3,4] The phase sequence of ZrO_2 at ambient pressure with increasing temperature is as follows: baddeleyite → tetragonal ZrO_2 ($P4_2/nmc$) → cubic ZrO_2 ($Fm3m$, fluorite).[5,6] A number of theoretical studies of ZrO_2 have been extensively performed[7–9] to understand its electronic, mechanical and structural properties. Zr_3O, which is important for slowing down hydrogen diffusion inside the bulk of the Zr alloy,[10] has also been identified at the oxide–metal interface in Zr alloys.[11,12] The closely related Ti–O system has six stable oxide phases: $P31c$-Ti_6O,[13] $P\bar{3}1c$-Ti_3O,[14] $P\bar{3}m1$-Ti_2O,[14] $Fm\bar{3}m$-TiO,[15] $R\bar{3}c$-Ti_2O_3[15] and rutile $P4_2mnm$-TiO_2,[16] while the Hf–O system has only one known stable phase: monoclinic $P2_1/c$-HfO_2[17] at 0 GPa. Can other compounds be stable in the Zr–O system? In our paper, we focus on searching for stable Zr–O compounds that may have been overlooked at 0 GPa and investigating the hardness trends of these phases.

II. Computational methodology

Searches for stable Zr–O compounds were done using the evolutionary algorithm (EA) as implemented in the USPEX code[18,19] in its variable-composition mode,[20] in conjunction with *ab initio* structure relaxations using density functional theory (DFT) within the PBE-GGA functional,[21] as implemented in the VASP package.[22] Evolutionary simulations of the Zr–O system were performed at 0 GPa with up to 20 atoms in the unit cell. The first generation of Zr–O structures was produced using the random symmetric algorithm,[19] all subsequent generations of Zr–O structures were produced in the following manner: 20% were generated randomly, and the rest by variation operators including heredity (40%), lattice mutation (20%), and transmutation (20%).

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The electron–ion interaction was described by the projector augmented-wave (PAW) pseudopotentials,[23] with $4s^2 4p^6 5s^2 4d^2$ and $2s^2 2p^4$ shells treated as valence for Zr and O, respectively. The plane-wave kinetic energy cutoff was chosen as 600 eV, and we used Γ-centered uniform k-point meshes to sample the Brillouin zone. A $19 \times 19 \times 19$ k-point grid was used to calculate the density of states (DOS). To compute phonons, we used the supercell method as implemented in the Phonopy code,[24] and the force constant matrices were computed using $2 \times 2 \times 2$ supercells.

III. Results and discussion

A. Crystal structure prediction and structural properties

The following compounds were found to be thermodynamically stable: $R\bar{3}$-Zr_6O, $R\bar{3}c$-Zr_3O, $P\bar{3}1m$-Zr_2O, $P\bar{6}2m$-ZrO, and $P2_1/c$-ZrO_2. Detailed Gibbs free energies of formation of Zr–O compounds under conditions of zero pressure and several temperatures are shown in Fig. 1. The hexagonal $P6_3/mmc$-Zr and magnetic solid oxygen were used to generate the convexhull at 0 GPa and 0 K. Our calculations indicated that the known monoclinic $P2_1/c$-ZrO_2 (baddeleyite) is the most stable structure of ZrO_2, which is in accordance with the experimental results.[25] Monoclinic ZrO_2 is not only the best known of these compounds, but also exists in the widest range of chemical potentials – unlike Zr_6O, Zr_3O, Zr_2O, and ZrO, which are stable only under strongly reducing conditions. This can explain why ZrO_2 is easier to be experimentally observed than other Zr–O compounds. For Zr_3O, the calculated results present here suggest that the experimental $R\bar{3}c$-Zr_3O[26] is the most stable structure, which is in agreement with the results of Zr_3O reported by Burton.[27] $P6_322$-Zr_3O (Fe_3N type), which was firstly reported by Holmberg and Dagerhamn,[28] exhibits very close but higher formation energy than $R\bar{3}c$-Zr_3O as depicted in Fig. 1(a) (open blue square). However, Holmberg and Dagerhamn[28] proposed the structure of $P6_322$-Zr_3O by means of X-ray diffraction; the structure of $P6_322$-Zr_3O was also confirmed using the neutron diffraction studies by Yamaguchi[29] as well as by Riabov[30]. Our calculated results reveal that no negative frequencies exist in the whole Brillouin zone in the calculated phonon dispersion for $P6_322$-Zr_3O, indicating that it is dynamically stable and it should be in a metastable phase at 0 K and 0 GPa in the framework of First-Principles DFT calculations. Moreover, we confirmed that $R\bar{3}c$-Zr_3O will transform into $P6_322$-Zr_3O at about 700 K. Therefore, the temperature changes may explain why the experiments were more inclined to find $P6_322$-Zr_3O. $Pn\bar{3}m$-Zr_2O (Cu_2O type) is experimentally reported by Khitrova and Klechkovskaya.[31] The formation enthalpy of $Pn\bar{3}m$-Zr_2O is 0.246 eV per atom higher than that of $P\bar{3}1m$-Zr_2O. This coupled with the fact that negative frequencies exist in the Brillouin zone of its calculated phonon dispersion indicates that $Pn\bar{3}m$-Zr_2O is an unstable phase at 0 K and 0 GPa.

In order to consider the effects of temperature on formation enthalpy (Fig. 1(b)), quasi-harmonic free-energy of hcp-Zr, Zr_6O, Zr_3O, Zr_2O, ZrO and ZrO_2 was calculated using the Phonopy code,[24] while for oxygen, we used the expression: $\mu_O(T,p^0) = 1/2[H(T,p^0,O_2) - H(0\text{ K},p^0,O_2)] - 1/2T[S(T,p^0,O_2) - S(0\text{ K},p^0,O_2)]$[32] to obtain the oxygen chemical potential with 0 K as the reference, as shown in Table 1. The enthalpy and entropy of O_2 were tabulated in thermochemical tables.[33] We took these values relative to zero Kelvin, and added to them our computed enthalpy of the magnetic O_2 molecule at 0 K (−4.88 eV per atom) to obtain the chemical potential of oxygen as a function of temperature. Except for ZrO_2 and Zr_3O, Zr_6O, Zr_2O and ZrO did not suffer from the elevated temperature phase transformation. From the convex hulls of the Zr–O system at zero pressure and different temperatures, we have computed the phase diagram of the Zr–O system in axes of temperature and oxygen chemical potential (Fig. 2), which can directly visualize the relative stability of these zircon oxides. Note the region of ZrO_2 in the calculated phase diagram (Fig. 2), our calculations indicate that $P2_1/c$-ZrO_2 will transform into $P4_2/nmc$-ZrO_2 at about 1680 K, which is a little higher than the experimental transition temperature of 1478 K.[25] $R\bar{3}c$-Zr_3O will transform into $P6_322$-Zr_3O at about 700 K and continue to be stable as the temperature increases to 2000 K. It turns out that Zr_6O and ZrO are thermodynamically stable up to 900 K and 1300 K,

Fig. 1 (a) Enthalpy of formation of Zr–O compounds at 0 GPa and T = 0 K. Open squares denote some notable experimental phases. (b) Gibbs free energy of formation for Zr–O compounds at 900 K, 1000 K, 1300 K, 1400 K and 2000 K and P = 0 GPa (for clarity, the O/(Zr + O) ratio from 0 (Zr) to 0.6667 (ZrO_2) was drawn). Open triangles represent unstable phases. For ZrO_2, $P4_2/nmc$-ZrO_2 is used at 2000 K ($P2_1/c$-ZrO_2 will transform into $P4_2/nmc$-ZrO_2 at 1680 K, basically in agreement with the experiment at 1478 K, ref. 25). Zr_3O shown in (b) should be $P6_322$-Zr_3O since $R\bar{3}c$-Zr_3O will transform into $P6_322$-Zr_3O at about 700 K.

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Table 1 $\mu_O(T, p^0)$ in the temperature range with 0 K as the reference at 1 atm (≈0 GPa)

T (K)	$\mu_O(T, p^0)$ (eV)	T (K)	$\mu_O(T, p^0)$ (eV)
100	−0.07	1100	−1.23
200	−0.17	1200	−1.36
300	−0.27	1300	−1.49
400	−0.38	1400	−1.62
500	−0.50	1500	−1.75
600	−0.61	1600	−1.88
700	−0.73	1700	−2.02
800	−0.85	1800	−2.16
900	−0.98	1900	−2.30
1000	−1.10	2000	−2.43

Fig. 2 Oxygen chemical potential–temperature phase diagram for the Zr–O system.

respectively. Zr_2O is still stable as the temperature increases up to 2000 K, which is higher than the experimental results obtained at 1270 K,[25] which is in agreement with the other calculated results.[27,34]

Structurally, Zr oxides fall into three groups: intercalated hcp-suboxides (Zr_6O, Zr_3O, and Zr_2O), intercalated ω-phase suboxide ZrO, and oxide ZrO_2. Structures of zirconium suboxides Zr_6O, Zr_3O, and Zr_2O are based on very similar principles, hexagonal close packing of Zr atoms, in which the O atoms fill 1/6, 1/3, and 1/2 of the octahedral voids, respectively. The O-centered octahedra tend to avoid each other. In the polyhedral representation of the structure of Zr_6O, the O-centered octahedra form "anti-corundum" layers (in these layers, 1/3 of the octahedra are filled by O atoms and 2/3 are empty), which alternate with O-free layers. The structure of Zr_3O is fully built of the "anti-corundum" layers, whereas the structure of Zr_2O displays alternating "anti-corundum" (with 1/3 filling of the octahedra) and "corundum" layers (with 2/3 filling of the octahedra). One can conjecture that these suboxides should easily absorb or desorb oxygen, transforming into one another without loss of single-crystallinity.

The structure of ZrO is rather unusual – it consists of Zr-graphene layers (Fig. 3(c)) stacked on top of each other (Zr–Zr distances within the layer are 3.08 Å and between the layers are 3.22 Å), as illustrated in Fig. 4(a). In the center of the big hexagonal void between the two graphene layers, there is an additional Zr atom surrounded by three oxygens (at a Zr–O distance of 2.16 Å), and each of these oxygens is also bonded to four other Zr atoms (at a distance of 2.28 Å). This structure, therefore, is built of a 3D-framework of short and strong Zr–O bonds, reinforced by rather strong Zr–Zr bonds. The former leads to high hardness, the latter may improve toughness due to semimetallic behavior. Moreover, the crystal structure of $P\bar{6}2m$-ZrO shares significant features with the structure of the well-known phase ω-Zr. The ω phase has been observed in some Ti-, Zr- and Hf-based alloys.[35,36] ω-Zr with the space group $P6/mmm$ is the high pressure allotrope of α-Zr (hcp structure, space group $P6_3/mmc$). ω-Zr has an interesting crystal structure related to the AlB_2 structure type; it has three atoms per unit cell and cell parameters a = 5.036 and c = 3.109, ref. 37 (c = 3.136, ref. 38). Zr atoms in both $P\bar{6}2m$-ZrO and ω-Zr have the same arrangement as atoms of Al and B in the AlB_2 structure, see Fig. 4. Xue *et al.* predicted that $P\bar{4}m2$-Zr_2O_3[39] is stable; however, we find that this phase is not energetically favorable at 0 GPa. It turns out to be metastable with respect to decomposition into $P\bar{6}2m$-ZrO and $P2_1/c$-ZrO_2 at 0 GPa. The weighted average lengths of Zr–Zr and Zr–O bonds in Zr–O compounds are plotted in Fig. 5.

Table 2 lists the detailed crystallographic data for Zr–O compounds at 0 GPa. Our variable-composition USPEX calculations

Fig. 3 Crystal structures of (a) $R\bar{3}$-Zr_6O, (b) $R\bar{3}c$-Zr_3O, (c) $P\bar{3}1m$-Zr_2O, (d) $P\bar{6}2m$-ZrO and (e) $P2_1/c$-ZrO_2. Green spheres-Zr; red spheres-O atoms. O-centered and Zr-centered polydedra are shown for Zr suboxides and ZrO_2, respectively.

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Fig. 4 Crystal structures of $P\bar{6}2m$-ZrO (a) and (c) for comparison ω-Zr (b and d). Green spheres-Zr_1; cyan spheres-Zr_2; red spheres-O atoms.

Fig. 5 Average bond lengths in Zr–O compounds.

reveal that the Zr–O binary system has five stable compounds ($R\bar{3}$-Zr_6O, $R\bar{3}c$-Zr_3O, $P\bar{3}1m$-Zr_2O, $P\bar{6}2m$-ZrO and $P2_1/c$-ZrO_2), see Fig. 1. Among these, $R\bar{3}$-Zr_6O, $P\bar{3}1m$-Zr_2O, and $P\bar{6}2m$-ZrO are hitherto unknown compounds. The structural stability of these novel Zr–O compounds has been checked by phonon calculations. As shown in Fig. 6, no imaginary phonon frequencies are detected throughout the Brillouin zone, indicating that these structures are all dynamically stable. It is notable that the vibrations of O atoms in the suboxides are decoupled from lattice modes, as shown in Fig. 5.

B. Mechanical properties of the Zr–O system

The elastic constants of $R\bar{3}$-Zr_6O, $R\bar{3}c$-Zr_3O, $P\bar{3}1m$-Zr_2O, $P\bar{6}2m$-ZrO and $P2_1/c$-ZrO_2 are summarized in Table 3. From the elastic constants, we have ascertained that all these phases satisfy the mechanical stability criteria.[40–42]

Compositional variations of the bulk (B), shear (G), Young's (E) modulus, G/B ratio, Poisson's ratio ν and hardness (H_ν) of

Table 2 Structural parameters of Zr–O compounds found using USPEX at ambient pressure

Compound	Space group	Enthalpy of formation (eV per atom)	Lattice constants (Å)	Wyckoff positions	x	y	z
Zr_6O	$R\bar{3}$	−0.79	a = 5.65	Zr 18f	0.337	0.003	0.419
			c = 15.64	O 3a	0.00	0.00	0.00
Zr_3O	$R\bar{3}c$	−1.73	a = 5.674	Zr 18e	0.326	0.993	0.083
			c = 15.697	O 6b	0.00	1.00	0.00
Zr_2O	$P\bar{3}1m$	−1.78	a = 5.654	Zr 6k	0.333	1.00	0.253
			c = 5.248	O 2c	0.333	0.667	0.00
				O 1b	0.00	1.00	0.50
ZrO	$P\bar{6}2m$	−2.61	a = 5.327	Zr 1b	0.00	1.00	0.50
			c = 3.218	Zr 2c	0.6667	0.333	0.00
				O 3g	0.406	0.00	0.50
ZrO_2	$P2_1/c$	−3.36	a = 5.220	Zr 4e	0.276	0.0436	0.710
			b = 5.280	O 4e	0.067	0.329	0.848
			c = 5.407	O 4e	0.450	0.757	0.976
			β = 99.67°				

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Fig. 6 Phonon dispersions of (a) $R\bar{3}$-Zr_6O (b) $P\bar{3}1m$-Zr_2O and (c) $P\bar{6}2m$-ZrO at 0 GPa.

Table 3 Calculated elastic constants C_{ij}, bulk modulus B, shear modulus G, Young's modulus E, Poisson's ratio ν, and hardness of Zr–O compounds and some literature values of ZrO_2. All properties are in GPa (except for dimensionless G/B and ν)

					ZrO_2		
Compound	Zr_6O	Zr_3O	Zr_2O	ZrO	This work	Calc.[9]	Expt.[43]
c_{11}	162	201	269	330	301	337	361
c_{22}					354	351	408
c_{33}	207	217	283	347	253	268	258
c_{44}	50	71	96	125	73	79	99.9
c_{55}					81	70	81.2
c_{66}					117	114	126
c_{12}	97	106	110	102	154	155	142
c_{13}	72	92	100	136	96	84	55
c_{14}	−3.3	16	−19				
c_{15}	8				40	26	−21.3
c_{23}					146	153	196
c_{25}					−4	−4	31.2
c_{35}					1.5	1.9	−18.2
c_{45}					−8	−14.6	−22.7
B_H	112	133	160	195	182	189	190
G_H	44	58	86	115	85	87	96
E	114	151	219	288	220	227	247
G/B	0.39	0.4	0.54	0.59	0.47	0.46	0.50
ν	0.33	0.3	0.27	0.25	0.3	0.3	0.28
H_ν	3	5	10	14	7.9	8.1	10

$R\bar{3}$-Zr_6O, $R\bar{3}c$-Zr_3O, $P\bar{3}1m$-Zr_2O, $P\bar{6}2m$-ZrO, $P2_1/c$-ZrO_2 are displayed in Fig. 7. When the ratio of O/(Zr + O) is 0.5, *i.e.* for ZrO, the mechanical properties B, G, E, G/B and hardness reach the peak values, while the ν value is minimum, as listed in Table 3. The large c_{33} values indicate that all the Zr–O compounds are highly incompressible along the c axis. The magnitude of variation in G and B is very large, as G and B values vary in ranges 40–120 GPa and 110–200 GPa, respectively. The criterion proposed by Pugh[44] and Poisson's ratio ν can be used to evaluate the brittle/ductile behavior of isotropic materials. According to Pugh's criterion, a material is brittle if $G/B > 0.57$. It seems natural to extend this criterion and expect that higher the value of G/B, the more brittle the materials would be. In the case of $G/B < 0.57$, a material is ductile. The calculations, as shown in Fig. 7(d) and (e), reveal that Zr_6O is more ductile than the other Zr–O compounds. In addition, the hardness comparison is drawn between $P6_322$-Zr_3O (a common experimental phase we mentioned above) and $R\bar{3}c$-Zr_3O – it

Fig. 7 Variation of B, G, E, G/B, ν and H with increasing O content in Zr–O compounds.

turns out that the hardness of $P6_322$-Zr_3O is 5 GPa, which is similar to the hardness of $R\bar{3}c$-Zr_3O. Vickers hardness was calculated according to Chen's model:[45]

$$H_V = 2 \times (k^2 \times G)^{0.585} - 3 \quad (1)$$

Once again, and surprisingly, we find that ZrO has the highest hardness, see Fig. 7(f). Combined with Fig. 7(a)–(c), we can also conclude that incorporation of oxygen interstitials

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Fig. 8 Orientation dependence of Young's moduli (in GPa) for (a) $P\bar{6}2m$-ZrO and (d) $P\bar{3}1m$-Zr_2O. Directional dependence of the torsion shear moduli (in GPa) for (b) $P\bar{6}2m$-ZrO and (e) $P\bar{3}1m$-Zr_2O. Anisotropy of the linear compressibility (in Å) for (c) $P\bar{6}2m$-ZrO and (f) $P\bar{3}1m$-Zr_2O.

Fig. 9 Normalized (per electron) total and partial densities of states for (a) $R\bar{3}$-Zr_6O, (b) $R\bar{3}c$-Zr_3O, (c) $P\bar{3}1m$-Zr_2O, (d) $P\bar{6}2m$-ZrO and (e) $P2_1/c$-ZrO_2. The Fermi energy is set to zero.

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Fig. 10 Band structures of (a) $R\bar{3}$-Zr_6O, (b) $R\bar{3}c$-Zr_3O, (c) $P\bar{3}1m$-Zr_2O, (d) $P\bar{6}2m$-ZrO and (e) $P2_1/c$-ZrO_2. The Fermi energy is set to zero.

Fig. 11 Electronic structure of $P\bar{6}2m$-ZrO in (a) DFT-GGA (black lines) and HSE06 (blue dashed lines), (b) GW (red solid lines). The Fermi energy is set to zero. (c) Dirac cone formed by the valence and conduction bands in the vicinity of the Dirac point. (d) First Brillouin zone with special k points: Γ(0 0 0), K(−0.333 0.667 0), and M(0 0.5 0).

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Fig. 12 (a) Crystal orbital Hamilton population (COHP) curves of Zr–O compounds. The dotted line at zero indicates the Fermi level. (b) Calculated integrated crystal orbital Hamiltonian population (–ICOHP) values of Zr–Zr, Zr–O and O–O interactions in Zr–O compounds.

improves hardness and increases brittleness, which is consistent with the experimental results.[46,47] However, we find it a big surprise that ZrO is harder than ZrO_2.

We further investigated the elastic anisotropy of $P\bar{6}2m$-ZrO (the highest bulk modulus, shear modulus and hardness among Zr–O compounds) and $P\bar{3}1m$-Zr_2O (the second hardest Zr–O compound), Young's modulus, torsion shear modulus and linear compressibility. The directional dependence of Young's modulus for hexagonal and trigonal crystals can be calculated using:

$$\frac{1}{E_{\text{hex}}} = s_{11}\left(1 - l_3^2\right)^2 + s_{33}l_3^4 + (2s_{13} + s_{44})l_3^2\left(1 - l_3^2\right) \quad (2)$$

$$\frac{1}{E_{\text{tri}}} = \left(1 - l_3^2\right)s_{11} + l_3^4 s_{33} + l_3^2\left(1 - l_3^2\right)(2s_{13} + s_{44}) + 2l_2l_3\left(3l_1^2 - l_2^2\right)s_{14}, \quad (3)$$

where s_{11}, s_{12}, *etc.*, are the elastic compliance constants and l_1, l_2, and l_3 are the direction cosines of a particular crystallographic orientation to coordinate axes x_1, x_2 and x_3, respectively.

To understand more deeply elasticity, as well as plastic deformation and crack behavior of $P\bar{6}2m$-ZrO and $P\bar{3}1m$-Zr_2O, it is necessary to study the dependence of the shear modulus on the stress direction. However, the shear modulus varies not only with the shear plane but also with the direction within that plane. Therefore, it is impossible to draw three-dimensional images to directly visualize the orientation-dependent shear modulus. Shear modulus is often measured by torsion shear modulus, which is an average of the shear plane, and it is related only to the direction of the shear plane and can be represented by three-dimensional diagrams. The torsion shear modulus (G_t) along an arbitrary direction can be calculated for hexagonal and trigonal crystals as follows:

$$\frac{1}{G_{\text{t(hex)}}} = s_{44} + \left[(s_{11} - s_{12}) - \frac{1}{2}s_{44}\right]\left(1 - l_3^2\right) + 2(s_{11} + s_{33} - 2s_{13} - s_{44})l_3^2\left(1 - l_3^2\right) \quad (4)$$

and

$$\frac{1}{G_{\text{t(tri)}}} = s_{11}\left(3l_1^2 - 2l_1^4 - 2l_2^4 + 3l_2^2 - 4l_1^2l_2^2\right) + 2s_{33}l_3^2\left(1 - l_3^2\right) + \frac{1}{2}s_{44}\left(l_1^2 + l_2^2 + 2l_3^2 - 4l_2^2l_3^2 - 4l_1^2l_3^2\right) - s_{12}\left(l_1^2 + l_1^2\right) - 4s_{13}l_3^2\left(l_1^2 + l_2^2\right) + 2s_{14}\left(2l_2^3l_3 - 5l_1^2l_2l_3 - l_1^2l_2l_3\right) \quad (5)$$

The linear compressibility of a crystal is the relative decrease in length of a line when the crystal is subjected to unit hydrostatic pressure. In general, it is anisotropic. For both hexagonal and trigonal systems, the directional dependence of linear compressibility β can be expressed as

$$\beta = (s_{11} + s_{12} + s_{13}) - (s_{11} + s_{12} - s_{13} - s_{33})l_3^2 \quad (6)$$

As shown in Fig. 8, both $P\bar{3}1m$-Zr_2O and $P\bar{6}2m$-ZrO exhibit a moderate amount of anisotropy of these quantities.

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C. Chemical bonding in the Zr–O system

Total and partial densities of states (DOSs) are presented in Fig. 9. For the total DOS of Zr_6O, Zr_3O and Zr_2O, there is no band gap in the DOSs at the Fermi level (E_F), indicating that these compounds are metals. A sharp valley (pseudogap) around the Fermi energy is a typical feature of the borderline between the bonding and antibonding states and an indication of electronic stabilization.[48–51] ZrO_2 is obviously an insulator with a wide band gap. Interestingly, and unlike the other compounds, ZrO is a semimetal with very few states at the Fermi level. The DOSs of Zr_6O, Zr_3O and Zr_2O below E_F are mainly contributed by the Zr-d, Zr-p and O-p orbitals and the interactions between the Zr-d occupied orbitals are responsible for metallicity. The highest occupied states in ZrO_2 are mainly derived from O-p orbitals. In addition, the valence band of Zr_6O, Zr_3O, Zr_2O and ZrO shown in Fig. 8 gradually shrinks with increasing O content. The valence band width reaches a minimum for ZrO.

Fig. 10 shows the band structures of Zr–O compounds. As shown in Fig. 11(a) and (b), semimetallic character[39] of $P\bar{6}2m$-ZrO is very clear (the overlap of the partially occupied valence band top and the conduction band bottom located at different high symmetry points A and Γ, respectively) in DFT, and was confirmed by calculations using the hybrid functional HSE06 and the GW approximation, respectively. We have also confirmed that semimetallicity of $P\bar{6}2m$-ZrO remains unchanged at positive and negative strain. One can observe that a very interesting massive Dirac-cone exists at the Γ-point, as shown in the green rectangle (Fig. 11(a)), slightly below (in the GGA and HSE06) or slightly above (in GW) the Fermi level. The 3D Dirac cone in the vicinity of the Γ-point is displayed in Fig. 10(c).

To identify the bonding and anti-bonding interactions in the Zr–O compounds, we have calculated the crystal orbital Hamilton population (COHP) and the integrated crystal orbital Hamilton population (ICOHP)[52] using the program TB-LMTO-ASA.[53] Bonding states indicated by negative values and anti-bonding states indicated by positive values (for convenience, we plot –COHP and –ICOHP, where bonding is indicated by positive values) are easy to observe in Fig. 12(a). Clearly, (1) the strength of Zr–Zr interactions falls rapidly with increasing O content, (2) peculiar and unique among these compounds is the combination of strong Zr–Zr and Zr–O bonding interactions in ZrO, which explains its superior mechanical properties.

IV. Conclusions

We have systematically searched the crystal structures of the Zr–O system at 0 GPa using the *ab initio* evolutionary algorithm USPEX. Three new stable compounds have been found, namely $R\bar{3}$-Zr_6O, $P\bar{3}1m$-Zr_2O and $P\bar{6}2m$-ZrO. Our results demonstrate that Zr_6O is more ductile than other zirconium oxides, while ZrO is the hardest one. The electronic structure of Zr_6O, Zr_3O, Zr_2O and ZrO shows that the disappearance of ductile Zr–Zr metallic bonds and the occurrence of Zr–O bonds are responsible for the increasing hardness. The peculiar combination of strong Zr–O and Zr–Zr bonds in $P\bar{6}2m$-ZrO enables it to have superior mechanical properties, such as bulk modulus B, shear modulus G, Young's modulus E and hardness H_ν. The recognition of the common structural features between $P\bar{6}2m$-ZrO and ω-Zr gives further insight into the physical properties and suggests that ZrO can be made as a hard semimetallic coating on the ω-Zr substrate.

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