



Ab initio study on the electronic and mechanical properties of ReB and ReC

Erjun Zhao^{a,c}, Jinping Wang^b, Jian Meng^a, Zhijian Wu^{a,*}

^a State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China

^b Department of Applied Chemistry, Qingdao Agricultural University, Qingdao 266109, PR China

^c Graduate School, Chinese Academy of Sciences, Beijing 100049, PR China

ARTICLE INFO

Article history:

Received 16 December 2008

Received in revised form

12 January 2009

Accepted 26 January 2009

Available online 5 February 2009

Keywords:

Rhenium carbide

Rhenium boride

Formation enthalpy

Elastic constants

Electronic properties

ABSTRACT

The structural, electronic, and mechanical properties of ReB and ReC have been studied by use of the density functional theory. For each compound, six structures are considered, i.e., hexagonal WC, NiAs, wurtzite, cubic NaCl, CsCl, and zinc-blende type structures. The results indicate that for ReB and ReC, WC type structure is energetically the most stable among the considered structures, followed by NiAs type structure. ReB–WC (i.e., ReB in WC type structure) and ReB–NiAs are both thermodynamically and mechanically stable. ReC–WC and ReC–NiAs are mechanically stable and becomes thermodynamically stable above 35 and 55 GPa, respectively. The estimated hardness from shear modulus is 34 GPa for ReB–WC, 28 GPa for ReB–NiAs, 35 GPa for ReC–WC and 37 GPa for ReC–NiAs, indicating that they are potential candidates to be ultra-incompressible and hard materials.

© 2009 Elsevier Inc. All rights reserved.

1. Introduction

Searching for materials with hardness comparable to or exceeding diamond has always fascinated humans. Superhard materials are known to be used in many applications, from cutting and polishing tools to wear-resistant coatings. In synthesizing and designing new superhard materials, besides the traditional B–C–N systems, transition metal carbides, borides and nitrides are also very attractive, in particular the 5d transition metal compounds because 5d transition metals have relatively high bulk modulus [1], but the shear strength is low due to the non-directional metallic bonding and therefore they have low hardness [2]. Therefore, it is expected that through the insertion of B, C, or N atom into the 5d transition metals, superhard materials might be formed by inducing the non-directional metallic bonding in pure 5d transition metals to highly directional covalent bonding in the corresponding carbides, borides or nitrides. In the following, we will briefly summarize the available studies for 5d transition metal carbides and borides.

For carbides, experimental studies include the elastic properties of HfC [3,4] and TaC [4,5] with NaCl type structure. The well-known WC has been known to crystallize in hexagonal phase [6] and has diverse applications such as machine tools in industry. In 1970s, ReC was synthesized at high temperature and high pressure in NaCl [7] and TiP [8] type structures. PtC has been

recently synthesized with NaCl structure [9]. On the theoretical side, the elastic properties of HfC and TaC with NaCl type structure were calculated by using the Debye–Grüneisen model combined with ab initio calculations and were reported to be hard materials [10]. PtC with NaCl type structure [11] and phase transformation from zinc-blende to NaCl structure [12] were studied by using the density functional theory. Other theoretical studies also include OsC with NaCl [13,14] and WC [14] type structures, ReC with NaCl [13], WC [15,16] and NiAs [15] type structures. It was found that ReC with WC type structures is the potential hard materials due to the high bulk and shear modulus [15,16]. On the other hand, for 5d transition metal borides, the experimental studies indicated that HfB was synthesized in NaCl type structure [17], TaB [18], WB [19] and IrB [20] in orthorhombic structure, as well as PtB in the anti-NiAs type structure [21]. In addition, the theoretical studies on WB, IrB, ReB and OsB with WC type structure were performed [22]. It was shown that the bulk moduli of these borides are comparable to that of cubic BN [22].

Recently, ReB₂ has been investigated both experimentally [23] and theoretically [24,25]. ReB₂ was synthesized via arc-melting under ambient pressure with hexagonal structure and the bulk modulus was 360 GPa [23]. The calculated shear modulus was around 290 GPa [24]. The measured Vickers hardness varies from 30 to 48 GPa upon decreasing the load from 4.9 to 0.49 N [23].

Since the superior mechanical properties of carbides and borides are closely related to their electronic structures, in this paper, the physical properties of ReC and ReB are studied by use of the density functional theory. For each compound, six structures are considered, i.e., NaCl (rocksalt), zinc-blende, CsCl, wurtzite,

* Corresponding author. Fax: +86 431 85698041.

E-mail address: zjwu@ciac.jl.cn (Z. Wu).

NiAs and WC type structures. In addition, anti-NiAs is also considered for ReB because from the previous study it was known that PtB crystallizes in anti-NiAs [21], and TiP type is considered for ReC because ReC in TiP type was synthesized experimentally [8].

2. Computational details

All the calculations conducted in this paper were performed within the CASTEP code [26], based on the density functional theory. The Vanderbilt ultrasoft pseudopotential [27], which describes the interaction of valence electrons with ions, was used with the cutoff energy of 600 eV for both ReB and ReC. The k-points of $8 \times 8 \times 8$ for NaCl and zinc-blende type, $12 \times 12 \times 12$ for CsCl type, $9 \times 9 \times 7$ for NiAs type, $12 \times 12 \times 11$ for WC type, $12 \times 12 \times 4$ for TiP type, and $10 \times 10 \times 6$ for wurtzite type were generated using the Monkhorst–Pack scheme [28]. The exchange and correlation functional were treated by the generalized gradient approximation (GGA–PBE) [29]. Formation enthalpy was calculated from $\Delta H = E(\text{ReX}) - E(\text{solid Re}) - E(\text{solid X})$ ($X = \text{B, C}$). The solid phase of B is from its α phase [30], and that of C is from the graphite. For the self-consistent field iterations, the convergence tolerance for geometry optimization was selected as the difference in total energy, the maximum ionic Hellmann–Feynman force, the stress tensor, and the maximum displacement being within 5.0×10^{-6} eV/atom, 0.01 eV/Å, 0.02 GPa, and 5.0×10^{-4} Å, respectively. The equivalent hydrostatic pressure is applied in pressure–enthalpy relationship study. The calculated bulk modulus B and shear modulus G are from the Voigt–Reuss–Hill's approximations [31–33]. They can be evaluated from the elastic stiffness constants as shown in Ref. [34]. Young's modulus E and Poisson's ratio ν are obtained by the following formulas:

$$E = 9BG/(3B + G), \quad \nu = (3B - 2G)/[2(3B + G)]$$

In the following, for clarity, we will use, for instance, ReB–WC to represent ReB in WC type structure.

3. Results and discussion

ReB. The calculated lattice parameters and elastic stiffness constants for ReB are listed in Table 1. The corresponding parameters of pure metal Re are also listed for comparison [35,36]. From Table 1, it is seen that for ReB–WC, the calculated lattice parameters $a = 2.872$ Å and $c = 2.903$ Å are close to $a = 2.863$ Å (deviating by 0.3%) and $c = 3.075$ Å (deviating by 5.9%) from the previous theoretical study [22], in particular for a axis. Our calculation gives small volume and thus larger bulk modulus 367 GPa compared with 346 GPa from the previous theoretical study [22]. ReB–WC and ReB–NiAs structures have negative formation enthalpy, indicating that they are thermodynamically stable at ambient conditions and might be accessed relative easily by experiment. ReB–WC is the most stable among the considered structures. For ReB–WC, ReB–NiAs, ReB–anti-NiAs, ReB–NaCl and ReB–CsCl structures, the calculated elastic stiffness constants indicate that they are mechanically stable because they satisfy the mechanical stability conditions [34]. For hexagonal phase with five independent elastic stiffness constants C_{11} , C_{33} , C_{44} , C_{12} and C_{13} , the mechanical stability conditions are

$$C_{33} > 0, \quad C_{44} > 0, \quad C_{12} > 0, \quad C_{11} > |C_{12}|, \quad (C_{11} + 2C_{12})C_{33} > 2C_{13}^2$$

While for cubic phase with three independent elastic stiffness constants C_{11} , C_{12} and C_{44} , they are

$$C_{11} > 0, \quad C_{44} > 0, \quad C_{11} > |C_{12}|, \quad (C_{11} + 2C_{12}) > 0$$

ReB–CsCl has the largest bulk modulus 386 GPa (Table 1), followed by ReB–WC with 367 GPa. These values are slightly larger than or comparable to 360 GPa of cubic boron nitride [2] and ReB_2 [23,24], as well as 372 GPa of pure Re [36]. For the calculated shear modulus, ReB–WC is the largest among the considered structures (248 GPa), followed by 210 GPa of ReB–NiAs. These values are smaller than ~ 290 GPa of ReB_2 [24]. This might be due to the absence of B–B bonding (available in ReB_2 , see Ref. [23]) in the considered ReB structures. From Table 1, it is also

Table 1

ReB. Formation enthalpy per formula unit ΔH (eV), lattice parameters a and c (Å), cell volume per formula unit V (Å³), elastic stiffness constants C_{ij} , bulk modulus B (GPa), shear modulus G (GPa), Young's modulus E (GPa), Poisson's ratio ν and Debye temperature θ_D (K) from various space groups: hexagonal NiAs ($P6_3/mmc$, No. 194), WC ($P-6m2$, No. 187), and wurtzite ($P6_3mc$, No. 186); cubic zinc-blende ($F-43m$, No. 216), CsCl ($Pm-3m$, No. 221) and NaCl ($Fm-3m$, No. 225).

	WC	NiAs	anti-NiAs	NaCl	CsCl	Wurtzite	Zinc-blende	hcp Re
ΔH	−0.58	−0.39	0.11	0.45	0.65	1.29	1.79	
a	2.872(2.863 ^a)	2.865	2.921	4.370	2.709	2.942	4.697	2.76 ^b
c	2.903(3.075)	5.876	5.564			6.483		4.46 ^b
V	20.7	20.9	20.6	20.9	19.9	24.3	25.9	
C_{11}	625	531	393	674	702			618.2 ^c
C_{33}	770	678	476					683.5 ^c
C_{44}	304	319	105	50	119			160.6 ^c
C_{12}	228	239	364	166	228			275.3 ^c
C_{13}	210	254	282					207.8 ^c
B	367(346)	357	346	335	386			372 ^b 367 ^d
G	248	210	48	103	157			178 ^d
E	608	526	138	280	415			461 ^d
ν	0.22	0.25	0.43	0.36	0.32			0.29 ^d
B/G	1.48	1.70	7.21	3.26	2.46			2.06
θ_D	600	554	271	383	479			

For ReB, anti-NiAs ($P6_3/mmc$, No. 194) structure are also considered. The corresponding data from the elemental hexagonal close packed (hcp) Re is also presented for comparison. The considered structures were arranged in the order of energy (ΔH).

^a Ref. [22], values in parenthesis of this column are from local density approximation (LDA) calculation.

^b Ref. [36], from experiment.

^c Ref. [35], from experiment.

^d Present work, calculated from the Voigt–Reuss–Hill's approximations based on the elastic stiffness constants.

seen that ReB–WC has the largest Young's modulus (608 GPa) and the smallest Poisson's ratio (0.22). The small Poisson's ratio suggests that Re–B bond in ReB–WC structure is more directional or has high degree of covalency. The above results suggest that ReB–WC structure is the hardest among the considered structures. The calculated B/G ratios are 1.48 and 1.70 for ReB–WC and ReB–NiAs, respectively, indicating that they are brittle. This is because a low (high) B/G ratio is related with brittleness (ductility), and the critical value is about 1.75 [37]. For instance, diamond has a B/G ratio 0.8 [2], while aluminum and cobalt have the B/G ratios 2.74 and 2.43, respectively [37]. Pure Re has also relatively large B/G ratio of 2.06 (Table 1) or 1.76 [37]. In a word, the above results indicate that ReB–WC and ReB–NiAs are potential candidates to be ultra-incompressible and hard materials.

Next, we have calculated the Debye temperature. It is known that as a fundamental parameter, Debye temperature correlates with many physical properties of solids, such as specific heat, elastic stiffness constants, and melting temperature. At low temperatures, the vibrational excitations arise solely from acoustic vibrations. Therefore, Debye temperature calculated from elastic stiffness constants at low temperatures is the same as that determined from specific heat measurements. The Debye temperature can be derived from the bulk modulus, shear modulus, and density of materials [24]. The calculated Debye temperature is the largest (600 K) for ReB–WC, followed by 554 K for ReB–NiAs. These values are much smaller than 860 K in ReB₂ [24]. It is also interesting to note that for diamond with B/G = 0.8 [2], the Debye temperature is 2230 K [38a]. While for aluminum, B/G = 2.74 [37], the Debye temperature is 428 K [38a].

ReC. The calculated lattice parameters and elastic stiffness constants for ReC are listed in Table 2. It is seen that all the considered structures are thermodynamically unstable due to the positive formation enthalpy. This indicates that high pressure and/or high temperature are/is necessary for the experimental synthesis. It is indeed noted that the ReC–TiP [8] and ReC–NaCl [7] structures were synthesized at high pressure and high temperature. Among the considered structures, ReC–WC is energetically the most stable phase. The relative stability order ReC–WC > ReC–NiAs > ReC–zinc-blende > ReC–NaCl and energy difference (–0.72, –0.62 and –0.20 eV/atom relative to ReC–NaCl) are the

same as that in the previous theoretical study [15]. From Table 2, it is interesting to note that the hexagonal structures are energetically more stable than the cubic ones. The calculated lattice parameters of ReC–WC and ReC–NiAs structures are in excellent agreement with the previous GGA calculations [15], matching each other within 0.3%. The calculated bulk and shear moduli are also close to each other (Table 2). The calculated elastic stiffness constants indicate that ReC–WC, ReC–NiAs, ReC–wurtzite, and ReC–CsCl structures are mechanically stable because they satisfy the mechanical stability criteria [34]. The calculated bulk modulus 442 GPa of ReC–CsCl is the largest among the considered structures, same as 442 GPa of diamond [2]. In addition, ReC–WC and ReC–NiAs have also relatively large bulk modulus, i.e., 434 GPa and 427 GPa, respectively. For the shear modulus, ReC–NiAs has the largest value (264 GPa), followed by 252 GPa for ReC–WC. This is in agreement with the previous theoretical study [16]. For ReC–CsCl, however, although it has the largest bulk modulus, the shear modulus is small (120 GPa). Thus, ReC–NiAs and ReC–WC would be very interesting and might be potential ultra-incompressible and hard materials. Compared ReC with ReB, it is seen that for each considered structures, ReC has smaller lattice parameters and larger bulk moduli than those in ReB. Based on Pugh's notion [37], ReC–WC and ReC–NiAs are brittle because the B/G ratio is 1.72 and 1.62, respectively, smaller than the critical value 1.75. This is similar to the situation in ReB–WC and ReB–NiAs. For ReC–WC and ReC–NiAs, the calculated Debye temperatures are 597 and 612 K, respectively, which are similar to the experimental values 593 ± 71 K of hard TaC in NaCl type [5] and 545 K of hard HfC in NaCl type structure [39]. Due to the superior mechanical properties, ReC–NiAs and ReC–WC might replace diamond in some applications such as in cutting processes.

In order to get insight into the chemical bonding, the total and partial density of states (DOS) of ReB–WC and ReC–WC structures are shown in Fig. 1. For the remaining structures, they are not shown since the obtained DOS patterns are similar. From Fig. 1, it is seen that both ReB–WC and ReC–WC are metallic due to the finite DOS at the Fermi energy level. For ReB–WC, the hybridization between B 2s orbital and Re 5d orbital can be seen in the energy region from –10.0 to –7.0 eV. At the energy region from

Table 2
ReC.

	WC	NiAs	TiP	Wurtzite	Zinc-blende	NaCl	CsCl
ΔH	0.52	0.72	1.27	1.43	1.56	1.96	2.25
a	2.852(2.850 ^a)	2.845(2.853 ^a)	2.853(2.84 ^b)	2.953	4.592	4.304 (4.33 ^c , 4.005 ^d)	2.655
c	2.787(2.786)	5.608(5.593)	11.209(9.85)	6.121			
V	19.6(19.6)	19.6(19.7)	19.8	23.1	24.2	19.9	18.7
C_{11}	776(796)	702(726)		272			1019
C_{33}	1001(1123)	942(993)		554			
C_{44}	198(195)	291(284)		33			31
C_{12}	227(242)	254(229)		247			153
C_{13}	231(192)	255(225)		324			
B	434(440)	427(422)	411	278	296	395(404)	442
G	252(223)	264(274)		25			120
E	634	656		71			330
ν	0.25	0.24		0.46			0.37
B/G	1.72	1.62		11.1			3.68
θ_D	599	612		197			417

For detailed expressions, see Table 1.

^a Ref. [15], values in parenthesis of these two columns are from GGA–PBE calculation.

^b Ref. [8], values in parenthesis of this column are from experiment.

^c Ref. [13], values in parenthesis of this column are from LDA calculation.

^d Ref. [7], values in parenthesis of this column are from experiment.

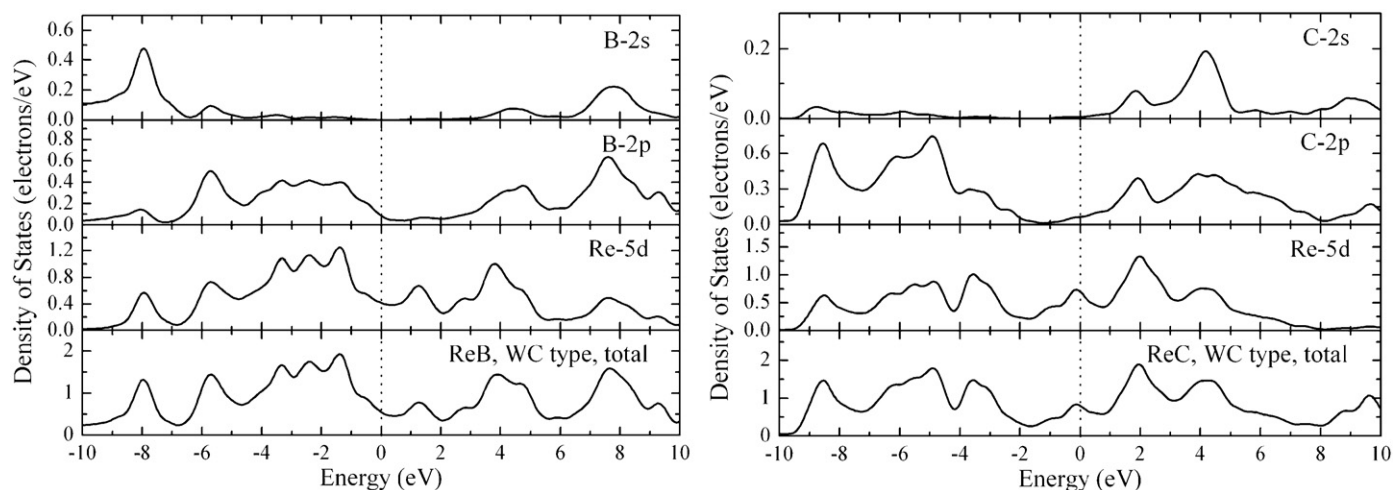


Fig. 1. Calculated total and partial density of states for ReB (left) and ReC (right) in WC type structure. The vertical dotted lines indicate the Fermi energy level.

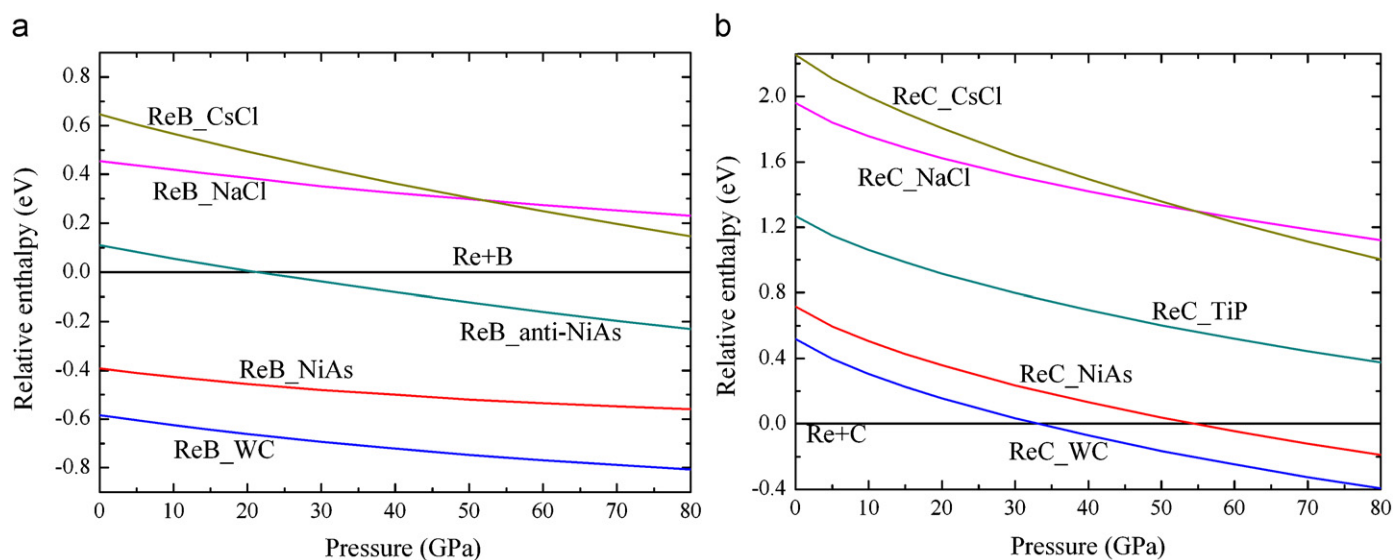


Fig. 2. (Color online) The enthalpy–pressure diagram for ReB (a) and ReC (b) from the selected structures compared with the initial reactants Re+B (a) and Re+C (b).

–7.0 to 0.0 eV, there exists a strong interaction between the B $2p$ and Re $5d$ orbitals. These indicate the covalent bonding between B and Re atoms. The contribution to Fermi energy level is mainly from Re $5d$ orbitals, with small B $2p$ orbitals and negligible B $2s$ orbitals.

For ReC–WC, in the energy region from –10.0 to 0.0 eV (Fig. 1), the contribution from C $2s$ orbitals is small. In fact, the main contribution of C $2s$ orbitals lies in the lower energy region (below –10.0 eV). From –10.0 to 0.0 eV, C $2p$ orbitals hybridize strongly with Re $5d$ orbitals, forming the covalent bonding. The DOS at Fermi energy level is contributed mainly from the Re $5d$ orbitals.

The relative enthalpies for ReB and ReC compared with the initial reactants as a function of pressure were investigated. It is seen from Fig. 2a that ReB–anti-NiAs structure becomes thermodynamically stable above 22 GPa. Whereas ReB–CsCl will surpass ReB–NaCl above 53 GPa and surpass the constituents and become thermodynamically stable at much higher pressure (above 112 GPa). For ReB–WC and ReB–NiAs structures, they are the thermodynamically stable phases below 80 GPa. ReB–WC is the most stable in the studied pressure range among the considered structures. From the previous studies, we noticed that the formation enthalpy of ReB_2 is also negative [24], which is

similar to the ReB–WC and ReB–NiAs structures. This reveals that ReB–WC might be synthesized with the same experimental conditions of ReB_2 [23], i.e., by use of the arc-melting method without extreme conditions.

For ReC, ReC–WC and ReC–NiAs become thermodynamically stable above 35 and 55 GPa, respectively (Fig. 2b). For the considered pressure range, ReC–WC is the most stable phase among the considered structures. On the other hand, if we choose diamond as the initial reactant at high pressure, instead of graphite, none of the structures is thermodynamically stable below 80 GPa. This indicates that the synthesis of ReC would be difficult, at least much more difficult than ReB. Recently, OsN_2 (Ref. [40]) and IrN_2 (Refs. [40,41]) have been synthesized by using the laser-heated diamond-anvil-cell techniques with the temperature exceeding 2000 K and pressures above 50 GPa. The same experimental conditions might be applied to the synthesis of ReC–WC since it becomes thermodynamically stable above 35 GPa.

It is known that microcracks are induced in ceramics due to the anisotropy of the coefficient of thermal expansion as well as elastic anisotropy. Since all the known crystals are essentially elastically anisotropic, the description of such an anisotropic

behavior is important in both engineering science and crystal physics. We thus calculated the percentage elastic anisotropy for polycrystalline materials which is defined as

$$A_B = (B_V - B_R)/(B_V + B_R) \quad \text{and}$$

$$A_G = (G_V - G_R)/(G_V + G_R)$$

in compressibility and shear, respectively. Where the subscripts V and R represent the Voigt and Reuss approximations. In these expressions, a value of zero corresponds to elastic isotropy and a value of 100% identifies the largest elastic anisotropy. For ReB–WC, $A_B = 0.3\%$, $A_G = 1.8\%$. This indicates that it is nearly isotropic in compressibility and there is less anisotropy in compressibility than in shear. Similar situation is also found for ReC–WC, in which $A_B = 0.6\%$ and $A_G = 2.4\%$.

In our previous study on 5d transition metal nitrides from LaN to AuN [42], we noticed that for ReN, ReN–WC is mechanically unstable. ReN–wurtzite is energetically the most stable among the considered structures. ReN–NiAs is the hardest phase with bulk modulus 418 GPa, shear modulus 238 GPa. It becomes thermodynamically stable above 5 GPa and the most stable phase above 42 GPa.

It is known that hardness is an important mechanical property of crystals and related to the elastic and plastic properties of a substance. An accurate determination of hardness is a complex issue involving a shear deformation, a volume compression, the creation and motion of dislocations, and even experimental measurement with different scales. Previous study suggests that shear modulus is known as a better indicator for hardness [2,43]. Thus, we have estimated the hardness of ReB–WC, ReB–NiAs, ReC–WC, and ReC–NiAs from the shear modulus. The estimated hardness based on the relationship between shear modulus and hardness [43] is 34 GPa for ReB–WC, 28 GPa for ReB–NiAs, 35 GPa for ReC–WC, and 37 GPa for ReC–NiAs. These values lie in the range 30–48 GPa of ReB₂ (Ref. [23]) and comparable to 35 ± 5 GPa of B₆O (Ref. [43]) and 30 ± 3 GPa of WC [43]. For ReC–WC and ReC–NiAs, the hardness 35 and 37 GPa are nearly the same as 36 and 38 GPa obtained based on the semiempirical method [15] (i.e., a method based on the bond volume and Mulliken population, see Ref. [44] for more details concerning the method). On the other hand, the valence electron density (VED) of ReB–WC 0.483 electrons/Å³ and ReC–WC 0.561 electrons/Å³ are larger than 0.476 electrons/Å³ of pure Re. Thus, it is the high VED and bond covalency, in particular the latter, that enhances the hardness significantly, compared with the hardness between 1.3 and 3.2 GPa of pure Re [23].

Finally, by using the relation $\gamma = (\pi^2 k_B^2/3)N(E_F)$ (k_B is the Boltzmann constant, and $N(E_F)$ is the DOS at the Fermi energy level), our calculated specific heat coefficient γ for pure Re is 1.94 mJ mol⁻¹ K⁻², in good agreement with the experimental value 2.3 mJ mol⁻¹ K⁻² [38b]. In addition, for ReB–WC, ReB–NiAs, ReC–WC, and ReC–NiAs, the calculated specific heat coefficients are 1.30, 1.53, 1.93, and 2.17 mJ mol⁻¹ K⁻², respectively. It is seen that the specific heat coefficient of ReB is smaller than that of ReC. They are also smaller than the specific heat coefficient 2.3 mJ mol⁻¹ K⁻² of pure Re.

4. Conclusions

The structural, electronic, and mechanical properties of ReB and ReC have been studied by use of the density functional theory. The results indicate that for ReB, ReB–WC and ReB–NiAs are thermodynamically stable, indicating that they can be synthesized relative easily by the experiment. Meanwhile, they are also mechanically stable. ReB–WC is the most stable among the considered structures for ReB and has large bulk modulus

367 GPa, shear modulus 248 GPa, Young's modulus 608 GPa, and small Poisson's ratio 0.22. The Debye temperature (600 K) is the largest among the considered structures.

For ReC, ReC–WC is energetically the most stable among the considered structures. It is mechanically stable and becomes thermodynamically stable above 35 GPa. This suggests that the synthesis of ReC would be more difficult than ReB and high pressure and/or high temperature are/is necessary for the synthesis of ReC. Nevertheless, the calculated bulk and shear moduli 434 and 252 GPa are very large, in particular the bulk modulus because it is close to 442 GPa of diamond. In addition, the large shear and bulk moduli 264 GPa and 427 GPa are also found in ReC–NiAs.

Due to the formation of covalent bonding in ReC and ReB, the estimated hardness 34 GPa for ReB–WC, 28 GPa for ReB–NiAs, 35 GPa for ReC–WC, and 37 GPa for ReC–NiAs are much larger than the hardness between 1.3 and 3.2 GPa of pure Re.

The above results show that ReB and ReC in both WC and NiAs type structures are potential candidates to be hard and ultra-incompressible materials. Hence, we suggest that the experimental exploration of these materials may be rather rewarding.

Acknowledgment

The authors thank the National Natural Science Foundation of China for financial support (Grant nos. 20773117, 20831004, 20671088).

References

- [1] J.J. Gilman, R.W. Cumberland, R.B. Kaner, *Int. J. Refractory Met. Hard Mater.* 24 (2006) 1.
- [2] J. Haines, J.M. Léger, G. Bocquillon, *Annu. Rev. Mater. Res.* 31 (2001) 1.
- [3] Q. Yang, W. Lengauer, T. Koch, M. Scheerer, I. Smid, *J. Alloys Comp.* 309 (2000) L5.
- [4] H.R. Brown, P.E. Armstrong, C.P. Kempter, *J. Chem. Phys.* 45 (1966) 547.
- [5] S.P. Dodd, M. Cankurtaran, B. James, *J. Mater. Sci.* 38 (2003) 1107.
- [6] J. Schuster, E. Rudy, H. Nowotny, *Monatsh. Chem.* 107 (1976) 1167.
- [7] S.V. Popova, *Acta Crystallogr. A* 31 (1975) S99.
- [8] S.V. Popova, L.G. Boiko, *High Temp. High Pressure* 3 (1971) 237.
- [9] S. Ono, T. Kikegawa, Y. Ohishi, *Solid State Commun.* 133 (2005) 55.
- [10] X.G. Lu, M. Selleby, B. Sundman, *Acta Mater.* 55 (2007) 1215.
- [11] C.Z. Fan, S.Y. Zeng, Z.J. Zhan, R.P. Liu, W.K. Wang, P. Zhang, Y.G. Yao, *Appl. Phys. Lett.* 89 (2006) 071913.
- [12] F. Peng, H.Z. Fu, X.D. Yang, *Solid State Commun.* 145 (2008) 91.
- [13] J.C. Grossman, A. Mizel, M. Côté, M.L. Cohen, S.G. Louie, *Phys. Rev. B* 60 (1999) 6343.
- [14] J.C. Zheng, *Phys. Rev. B* 72 (2005) 052105.
- [15] Z.W. Chen, M.X. Gu, C.Q. Sun, X.Y. Zhang, R.P. Liu, *Appl. Phys. Lett.* 91 (2007) 061905.
- [16] Y.X. Wang, *Phys. Stat. Solidi (RRL)* 2 (2008) 126.
- [17] O.I. Shulishova, I.A. Shcherbak, *Inorg. Mater.* 3 (1967) 1304.
- [18] R. Kiessling, *Acta Chem. Scand.* 3 (1949) 603.
- [19] E. Rudy, F. Benesovsky, L. Toth, *Z. Metallkd.* 54 (1963) 345.
- [20] P. Rogl, H. Nowotny, F. Benesovsky, *Monatsh. Chem.* 102 (1971) 678.
- [21] B. Aronsson, E. Stenberg, J. Åselius, *Acta Chem. Scand.* 14 (1960) 733.
- [22] D. Music, J.M. Schneider, *Scr. Mater.* 52 (2005) 29.
- [23] H.-Y. Chung, M.B. Weinberger, J.B. Levine, A. Kavner, J.-M. Yang, S.H. Tolbert, R.B. Kaner, *Science* 316 (2007) 436.
- [24] X.F. Hao, Y.H. Xu, Z.J. Wu, D.F. Zhou, X.J. Liu, X.Q. Cao, J. Meng, *Phys. Rev. B* 74 (2006) 224112.
- [25] R.F. Zhang, S. Veprek, A.S. Argon, *Appl. Phys. Lett.* 91 (2007) 201914.
- [26] M.D. Segall, P.J.D. Lindan, M.J. Probert, C.J. Pickard, P.J. Hasnip, S.J. Clark, M.C. Payne, *J. Phys. Condens. Matter* 14 (2002) 2717.
- [27] D. Vanderbilt, *Phys. Rev. B* 41 (1990) 7892.
- [28] H.J. Monkhorst, J.D. Pack, *Phys. Rev. B* 13 (1976) 5188; J.D. Pack, H.J. Monkhorst, *Phys. Rev. B* 16 (1977) 1748.
- [29] J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 77 (1996) 3865.
- [30] G. Will, B. Kiefer, *Z. Anorg. Allg. Chem.* 627 (2001) 2100.
- [31] W. Voigt, *Lehrbuch der Kristallphysik*, Teubner, Leipzig, 1928.
- [32] A. Reuss, *Z. Angew. Math. Mech.* 9 (1929) 49.
- [33] R. Hill, *Proc. Phys. Soc. London* 65 (1952) 350.
- [34] Z.J. Wu, E.J. Zhao, H.P. Xiang, X.F. Hao, X.J. Liu, J. Meng, *Phys. Rev. B* 76 (2007) 054115.

- [35] D.R. Lide, CRC Handbook of Chemistry and Physics, 86th ed., CRC Press, Florida, 2005–2006, pp. 12–37.
- [36] J. Donohue, The Structures of the Elements, Wiley, New York, 1974, pp. 191–199.
- [37] S.F. Pugh, Philos. Mag. 45 (1954) 823.
- [38] [a] C. Kittel, Introduction to Solid State Physics, eighth ed., Chinese ed., Chemical Industry Press, Beijing China, 2005, p. 86.
[b] C. Kittel, Introduction to Solid State Physics, eighth ed., Chinese ed., Chemical Industry Press, Beijing China, 2005, p. 105.
- [39] F.I. Ajami, R.K. MacCrone, J. Less-Common Met. 38 (1974) 101.
- [40] A.F. Young, C. Sanloup, E. Gregoryanz, S. Scandolo, R.J. Hemley, H.-K. Mao, Phys. Rev. Lett. 96 (2006) 155501.
- [41] J.C. Crowhurst, A.F. Goncharov, B. Sadigh, C.L. Evans, P.G. Morrall, J.L. Ferreira, A.J. Nelson, Science 311 (2006) 1275.
- [42] E.J. Zhao, Z.J. Wu, J. Solid State Chem. 181 (2008) 2814.
- [43] D.M. Teter, MRS Bull. 23 (1998) 22.
- [44] F.M. Gao, Phys. Rev. B 73 (2006) 132104.