Prediction of a superhard material of ReN_4 with a high shear modulus*

Zhao Wen-Jie(赵文杰), Xu Hong-Bin(许红斌), and Wang Yuan-Xu(王渊旭)†

Institute for Computational Materials Science, School of Physics and Electronics, Henan University, Kaifeng 475004, *China*

(Received 2 April 2009; revised manuscript received 5 May 2009)

Using first-principles calculations, this paper systematically investigates the structural, elastic, and electronic properties of ReN_4. The calculated positive eigenvalues of the elastic constant matrix show that the orthorhombic *Pbca* structure of ReN_4 is elastically stable. The calculated band structure indicates that ReN_4 is metallic. Compared with the synthesized superhard material WB_4, it finds that ReN_4 exhibits larger bulk and shear moduli as well as a smaller Poisson's ratio. In addition, the elastic constant c_{44} of ReN_4 is larger than all the known 5d transition metal nitrides and borides. This combination of properties makes it an ideal candidate for a superhard material.

Keywords: bulk modulus, shear modulus, hardness, elastic properties
PACC: 6220D, 7115A, 7115M

1. Introduction

Much effort has been made searching for new superhard materials during the past decade. Scientific attempts to synthesize or theoretically predict new superhard materials are focused on two classes of superhard materials. The first one is the compounds formed by the light elements (LEs) B, C, N, and O, such as diamond, cubic boron nitride (*c*-BN), and carbon nitrides etc.[1−4] The second one is the borides, carbides, nitrides, and oxides of transition metals (TMs).[5−22] The main difference in composition between the two classes of materials is that the first is formed by LEs while the second by the TM elements and LEs. In the second class, the TM elements have high valence electron density and the interstitial atoms such as boron, carbon, nitrogen, and oxygen are small and strong bond forming elements. It is well known that two designed parameters are of importance for the selection of superhard TM compounds, i.e., a high valence electron density of TM and the presence of directional covalent bonding. Applying this idea, Gu *et al.*[21] have synthesized the boron-rich compounds OsB, Os_2B_3, OsB_2, RuB, RuB_2, WB_2, and WB_4. Their experimental results show that the Vicker's hardness value (HV) (46.2 GPa) for WB_4 is in the order of *c*-BN[23,24] and the recently reported value for ReB_2 (48 GPa).[25] In addition, they found that the hardness of the material increases with increasing B content. For example, the HVs for OsB, Os_2B_3, and OsB_2 are 14.4 GPa, 21.8 GPa, and 23.5 GPa, respectively. Then, Wang *et al.*[26] reveal the origin of the high hardness for WB_4 by first-principles calculations and further predict that five other TMB compounds within the WB_4 structure are potential superhard materials. Furthermore, their calculations indicate that incorporating B into TMs does not significantly change the high electron densities and the strong covalent bonding between LEs is necessary for high hardness. Based on the above experimental and theoretical explorations, the best way of synthesizing new superhard materials could be an extensive search for LE-rich TM compounds, where LE–LE bonds are easily formed. In this study, first-principles calculations on the structural, elastic, and electronic properties of ReN_4 were performed systematically. Our calculations show that ReN_4 exhibits large bulk and shear moduli as well as a small Poisson's ratio and is expected to be a superhard material.

The initial structure model derives from the related compound of ReP_4,[27] because chemically related compounds often have a similar structure. For example, both PtN_2[17] and PtP_2[28] have the pyrite structure while IrN_2[8,9] and IrP_2[29] possess the monoclinic structure. Therefore, it is valuable to study ReN_4 with the orthorhombic *Pbca* structure of ReP_4.[27]

*Project supported by the Program for Science and Technology Innovation Talents in Universities of Henan Province, China (Grant No. 2009HASTIT003), the Foundation of Science and Technology Department of Henan Province, China (Grant No. 082300410010), and Scientific Research Foundation for the Returned Overseas Chinese Scholars, Ministry of Education of China.
†Corresponding author. E-mail: wangyx@henu.edu.cn
© 2010 Chinese Physical Society and IOP Publishing Ltd

2. Computational detail

The calculations presented in this study were performed within the density functional theory, using the projector-augmented wave (PAW) method.[30,31] We used the Vienna *ab initio* simulation program (VASP) computer code,[32−34] which implements the method. The local density approximation (LDA)[35] was used with the PAW potential. The structure was optimized with the conjugate-gradient algorithm method. A plane wave cutoff energy of 500 eV was employed throughout. All atoms were fully relaxed with the force on each ion less than 5 meV/Å(1 Å=0.1 nm). The calculations were performed by using a (7,5,4) Monkhorst–Pack mesh which corresponds to 70 k-points in the irreducible Brillouin zone of the orthorhombic *Pbca* structure ReN_4. Furthermore, increasing the cutoff energy to 600 eV and the number of k-points to (9,7,6) changes the lattice constants less than 0.05%, indicating that these calculations are reliable.

We use the strain-stress method to obtain the elastic constants of ReN_4. The elastic constants are listed in Table 1. From the calculated c_{ij}, the polycrystalline bulk modulus B, shear modulus G, Young's modulus E, and Poisson's ratio ν were further estimated by using the Voigt–Reuss–Hill approximation.[36]

Table 1. Calculated elastic constants c_{ij}, Poisson's ratio ν, Young's modulus E, bulk modulus B, and shear modulus G of ReN_4.

	c_{11}	c_{12}	c_{13}	c_{22}	c_{23}	c_{33}	c_{44}	c_{55}	c_{66}	ν	E	B	G
	/GPa										/GPa		
WB_4 (Ref. [26])	448	282	250			496	179			0.33	342.4	328.2	129.1
ReN_4	465	141	133	700	296	881	509	78	97	0.24	526.7	335.3	212.7

3. Results and discussions

As is well known, hardness is related to the elastic and plastic properties of a material. A superhard material should have a high shear modulus to restrict deformation in a direction different from the applied load besides a high bulk modulus to support the volume decrease caused by an applied load. The bulk modulus depends mainly on the valence electron density and is less related to structural details. Thus, it is necessary to calculate the valence electron density of ReN_4 firstly. As shown in Table 2, our calculated valence electron densities for Re and ReN_4 are 0.476 and 0.462 electrons/Å^3, respectively. These values show that incorporating N into Re almost does not change the high electron density, indicating the low compressible property of ReN_4. The valence electron density (0.462 electrons/Å^3) for ReN_4 is very close to WB_4 (0.465 electrons/Å^3).[26] The WB_4 has been demonstrated to be a superhard material both experimentally and theoretically.[21,26] Thus, ReN_4 is expected to show a low compressibility and to be a superhard material. Figure 1 shows the optimized orthorhombic *Pbca* structure of ReN_4.

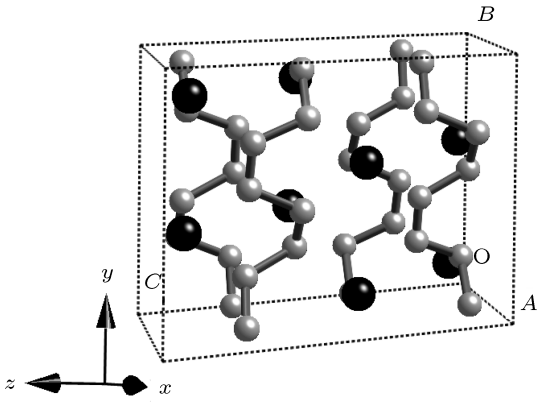


Fig. 1. Orthorhombic structure of ReN_4 with space group *Pbca*. The large and small spheres represent Re and N atoms, respectively.

Table 2. Calculated equilibrium lattice parameters a, b, c, cell volume (V), and valence electron densities (ρ) of ReN_4.

	a/Å	b/Å	c/Å	V/Å^3	ρ/(electrons/Å^3)
ReN_4	5.089	7.274	8.892	329.07	0.462

As listed in Table 1, the bulk modulus 335.3 GPa and shear modulus 212.7 GPa for ReN_4 are larger than the corresponding values of 328.2 GPa and 129.1 GPa for WB_4.[26] In particular, the shear modulus (212.7 GPa) for ReN_4 is about two times that of

WB_4 (129.1 GPa). The bulk modulus measures the resistance of a solid to volume change. The shear modulus, a measurement of resistance to shape change, is more pertinent to hardness. As Chung *et al.*[37] said: 'incompressibility (the reciprocal of bulk modulus) is a necessary but insufficient attribute of a hard material.' The shear modulus is indeed a significantly better qualitative predictor of hardness than the bulk modulus, and a linear relationship is observed between the hardness and shear modulus.[37] Now the shear modulus of ReN_4 is about two times of that of WB_4, it is to be expected that the hardness of ReN_4 is higher than WB_4. Not only is the hardness related to the bulk and shear moduli but it is also related to the elastic constant c_{44}, which is the most important parameter indirectly governing the indentation hardness. The elastic constant c_{44} for ReN_4 (509 GPa) is so large in comparison with known superhard materials such as ReB_2,[11−13] PtN_2,[17−19] and WB_4[26] that its resistance to the shear stress should be very strong, which is very consistent with the large shear modulus (212.7 GPa). In the *Pbca* structure of ReN_4, the N atoms form pseudo-N_2 molecules with the nearest N–N distance of 1.30 Å and next-nearest N–N distance of 1.44 Å. More importantly, the arrangement of these pseudo-N_2 molecules runs generally with the (100) plane, which results primarily in the largest elastic constant c_{44} of the known 5d TM nitrides and borides. The value of the Poisson's ratio is an indication of the degree of directionality of the covalent bonds. The smaller Poisson's ratio for ReN_4 (0.24) compared to WB_4 (0.33)[26] indicates a stronger degree of covalent bonding resulting in higher hardness. The elastic anisotropy of a crystal can also be measured by the percentage anisotropy in compressibility and shear: $A_B = (B_V - B_R)/(B_R + B_V)$ and $A_G = (G_V - G_R)/(G_R + G_V)$. A value of 0 represents elastic isotropy and a value of 1 represents the maximum anisotropy. The values of A_B and A_G are calculated to be 4.91% and 11.14% for ReN_4, respectively. So ReN_4 exhibits a relatively high degree of isotropy in compressibility and shear. We calculated the eigenvalues of the elastic constant matrix and found that all eigenvalues are positive, indicating that ReN_4 is elastically stable.

To gain some insight into the electronic properties of ReN_4, we calculated its band structure and total density of states (DOS). From Fig. 2, ReN_4 is metallic because of some bands crossing the Fermi level. The total and partial DOS of ReN_4 is plotted in Fig. 3. As seen in Fig. 3, the DOS distribution of ReN_4 manifests a typical stability effect by the formation of a pseudogap, which contributes to its stability. ReN_4 was found to exhibit a larger bulk modulus, a larger shear modulus, and a smaller Poisson's ratio compared to WB_4. The WB_4 has been demonstrated to be a superhard material both experimentally and theoretically.[21,26] In addition, the elastic constant c_{44} of ReN_4 is larger than all the synthesized 5d TM nitrides and borides. Therefore, ReN_4 is expected to be a superhard material.

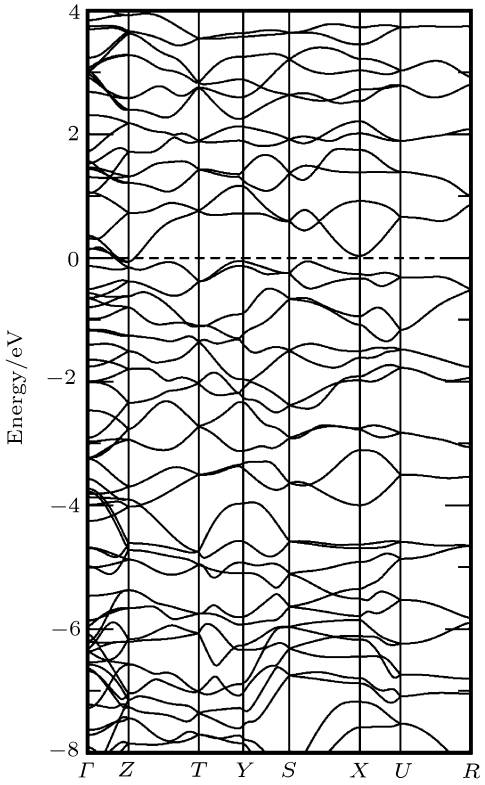


Fig. 2. Band structure of orthorhombic ReN_4. The high symmetry k points Z, T, Y, S, X, U, and R in the figure represent the points (0, 0, 1/2), (−1/2, 0, 1/2), (−1/2, 0, 0), (−1/2, 1/2, 0), (0, 1/2, 0), (0, 1/2, 1/2), and (−1/2, 1/2, 1/2), respectively.

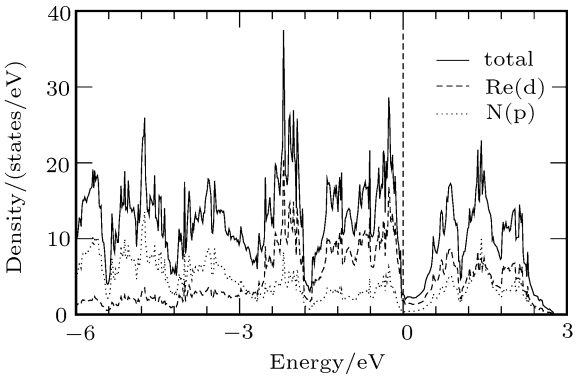


Fig. 3. Total and partial DOS of ReN_4. The Fermi level is at zero.

4. Conclusion

The structural, elastic, and electronic properties of ReN_4 have been investigated by using first-principles calculations. All positive eigenvalues of the elastic constant matrix show that the orthorhombic *Pbca* structure of ReN_4 is elastically stable. ReN_4 was found to exhibit larger bulk and shear moduli as well as a smaller Poisson's ratio in comparison with the synthesized superhard material WB_4. The smaller Poisson's ratio of ReN_4 means stronger directional bonding in it, which partially contributes to its high hardness. The calculated band structure shows that ReN_4 is metallic and its high stability can be attributed to the formation of a pseudogap near the Fermi level. In addition, the elastic constant c_{44} of ReN_4 is the largest of the known 5d TM nitrides and borides. So, we have good grounds for believing that ReN_4 is potentially a superhard material. We hope that our calculations can stimulate further experimental investigations on the technologically important nitrogen-rich compounds.

References

[1] Sun H, Jhi S H, Roundy D, Cohen M L and Louie S G 2001 *Phys. Rev.* B **64** 094108
[2] Teter D M 1998 *MRS Bull.* **23** 22
[3] Teter D M and Hemley R J 1996 *Science* **271** 53
[4] Li Q, Wang M, Oganov A R, Cui T, Ma Y M and Zou G T 2009 *J. Appl. Phys.* **105** 053514
[5] Wang S Y, Duan G Y, Qiu J H, Jia Y and Chen L Y 2006 *Acta. Phys. Sin.* **55** 1979 (in Chinese)
[6] Liang Y C, Guo W L and Fang Z 2007 *Acta. Phys. Sin.* **56** 4847 (in Chinese)
[7] Zhao W J and Wang Y X 2009 *Chin. Phys.* B **18** 3934
[8] Wang Y X, Arai M, Sasaki T and Fan C Z 2007 *Phys. Rev.* B **75** 104110
[9] Wu Z J, Zhao E J, Xiang H P, Hao X F, Liu X J and Meng J 2007 *Phys. Rev.* B **76** 054115
[10] Young A F, Sanloup C, Gregoryanz E, Scandolo S, Hemley R J and Mao H K 2006 *Phys. Rev. Lett.* **96** 155501
[11] Hao X F, Xu Y H, Wu Z J, Zhou D F, Liu X J, Cao X Q and Meng J 2006 *Phys. Rev.* B **74** 224112
[12] Liang Y C and Zhang B 2007 *Phys. Rev.* B **76** 132101
[13] Wang Y X 2007 *Appl. Phys. Lett.* **91** 101904
[14] Cumberland R W, Weinberger M B, Gilman J J, Clark S M, Tolbert S H and Kaner R B 2005 *J. Am. Chem. Soc.* **127** 7264
[15] Wang Y X 2008 *Phys. Stat. Sol.* **2** 126
[16] Gou H Y, Hou L, Zhang J W and Gao F M 2008 *Appl. Phys. Lett.* **92** 241901
[17] Yu R, Zhan Q and Zhang X F 2006 *Appl. Phys. Lett.* **88** 051913
[18] Gou H Y, Hou L, Zhang J W, Sun G F, Gao L H and Gao F M 2006 *Appl. Phys. Lett.* **89** 141910
[19] Yu R and Zhang X F 2005 *Phys. Rev.* B **72** 054103
[20] Guo X J, Xu B, He J L, Yu D L, Liu Z Y and Tian Y J 2008 *Appl. Phys. Lett.* **93** 041904
[21] Gu Q F, Krauss G and Steurer W 2008 *Adv. Mater.* **20** 3620
[22] Zhang M, Wang M, Cui T, Ma Y M, Niu Y L and Zou G T 2008 *J. Phys. Chem. Solids* **69** 2096
[23] Sung C M and Sung M 1996 *Mater. Chem. Phys.* **43** 1
[24] Brazhkin V V, Lyapin A G and Hemley R J 2002 *Phil. Mag.* **82** 231
[25] Chung H Y, Weinberger M B, Levine J B, Kavner A, Yang J M, Tolbert S H and Kaner R B 2007 *Science* **316** 436
[26] Wang M, Li Y W, Cui T, Ma Y M and Zou G T 2008 *Appl. Phys. Lett.* **93** 101905
[27] Jeitschko W and Rühl R 1979 *Acta Cryst.* **35** 1953
[28] Lukehart C M, Milne S B and Stock S R 1988 *Chem. Mater.* **10** 903
[29] Kjekshus A 1971 *Acta Chem. Scand.* **25** 411
[30] Kresse G and Joubert D 1999 *Phys. Rev.* B **59** 1758
[31] Blöchl P E 1994 *Phys. Rev.* B **50** 17953
[32] Kresse G and Hafner J 1993 *Phys. Rev.* B **47** 558
[33] Kresse G and Hafner J 1994 *J. Phys.: Condens. Matter* **6** 8245
[34] Kresse G and Furthmüller J 1996 *Phys. Rev.* B **54** 11169
[35] Ceperley D M and Alder B J 1980 *Phys. Rev. Lett.* **45** 566
[36] Hill R 1952 *Proc. Phys. Soc. London* **65** 349
[37] Chung H Y, Weinberger M B, Yang J M, Tolbert S H and Kaner R B 2008 *Appl. Phys. Lett.* **92** 261904