

Prediction of New Superhard Boron-Rich Compounds

Faming Gao,* Xiujuan Qin, Liqin Wang, Yunhua He, Guifang Sun, Li Hou, and Wenyin Wang

Department of Chemical Engineering, Yanshan University, Qinhuangdao 066004, China

Received: May 15, 2005; In Final Form: June 7, 2005

Boron solids exhibit a fascinating geometric and electronic structure. The properties of α -rhombohedral boron can be significantly changed by the addition of other atomic constituents. It is found that Pauling's bond valence principle plays an important role in designing boron-rich semiconductors. We have designed the novel boron-rich phases $B_{12}N_2X$ ($X = Zn, Cd, Be$) with the boron carbide type structure by combining Pauling's bond valence principle with first-principles techniques. Their energy gaps, bulk moduli, microhardnesses, and total energies have been calculated. The results show that they are new superhard materials and potential semiconductors. It has been elucidated why $B_{12}N_2$ is metallic but $B_{12}N_2Be$ is a semiconductor. This should open up new potential areas for predicting novel boron-rich compounds for industrial applications.

1. Introduction

How to rationally design new materials with exceptional properties on paper is the central challenge to modern materials science.¹ Once a promising new material has been predicted, experimentalists will be interested and attempt to synthesize it. Solid carbon nitride is an example.^{2–4}

Boron-rich compounds have been the subject of numerous investigations because of their novel scientific properties and potential technical applications.^{5–13} They hold a special place within chemistry due to their electron-deficient bonding. The properties of α -rhombohedral boron can be significantly changed by the addition of other atomic constituents. $B_{12}O_2$ ¹¹ and $AlMgB_{14}$ ¹⁴ are examples whose hardnesses were claimed to approximate that of cubic BN. However, until now no new boron-rich phases with higher hardnesses have been predicted or synthesized.

Because of the 5-fold rotational symmetry at the individual B atoms, the B_{12} icosahedra pack rather inefficiently; see Figure 1. In Figure 1, dotted lines show the three-center bonds between the six equatorial boron atoms in each icosahedron to six other icosahedra in the same sheet at 2.025 Å. The sheets are stacked so that each icosahedron is bonded by six two-center B–B bonds. B_{12} units in the layer above are centered over "1", and those in the layer below are centered under "2".¹⁵ The structure of α -rhombohedral boron contains a huge hole along the c -axis between the icosahedra. Most chemical doping takes place in the hole. In the boron carbide structure the huge hole accommodates three-atom chains. In the structures of $B_{12}X_2$ ($X = O, P, As$) the X atoms form pairs instead of three-atom chains.¹²

To design a semiconductor material by adding atoms to boron icosahedra, we find that Pauling's bond valence principle¹⁶ should be helpful. So far, no serious investigation has been made of icosahedral bonding along this line of thought for searching for new materials. According to Pauling's rule, if we consider a structure in which a cation A, carrying a charge $+ze$, is coordinated by n anions X, then each A–X bond is said to have an bond valence of z/n . In a stable coordinated structure the total bond valence of the bonds that reach an anion from all

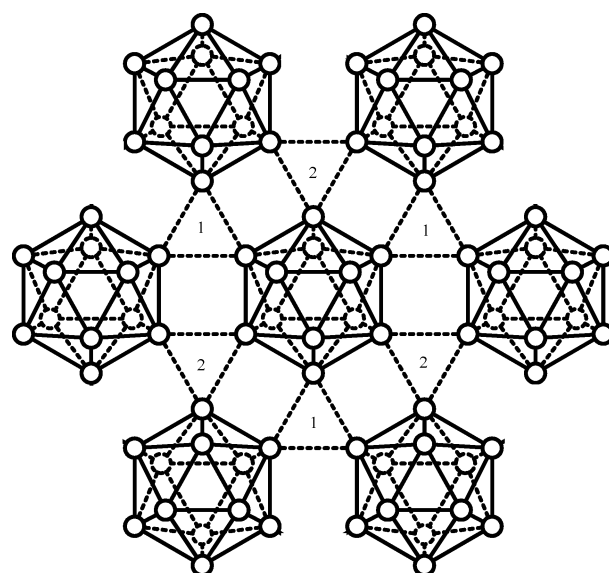


Figure 1. Basal plane of α -rhombohedral boron showing close-packed arrangement of B_{12} icosahedra. The dotted triangles denoted "1" and "2" show the three-center bonds between the six equatorial boron atoms in each icosahedron to six other icosahedra.

the neighboring cations is equal to the charge of the anion. In ref 17, we proposed a novel superhard material $B_{12}N_2Be$. Here we will further elucidate the designing mechanism based on Pauling's bond valence principle and predict more promising boron-rich semiconductors.

2. Theoretical Analysis

The 36 valence electrons of each B_{12} unit are distributed as follows: 26 electrons form the 10 three-center/two-electron bonds (denoted BBB1) and three normal two-center/two-electron bonds (denoted BB1) within the icosahedron and six electrons share with six other electrons from six neighboring icosahedra in adjacent planes to form the rhombohedrally directed normal two-center/two-electron bonds (denoted BB2); this leaves four electrons, which is just the number required for contribution to the six equatorial three-center/two-electron bonds ($6 \times 2/3 =$

* Corresponding author. E-mail: fmgao@ysu.edu.cn.

TABLE 1: Optimized Parameters, Energy Gaps, Bulk Modulus B , Microhardness, and Total Energy E_{total} of $\text{B}_{12}\text{N}_2\text{X}$ ($\text{X} = \text{Zn}$, Cd , Be) and Other Boron-Rich Phases Calculated by Using the LDA Approach of Local DFT with Pseudopotentials and Plane Wave Basis Set (Kinetic Energy Cutoff 280 eV)

	$\text{B}_{12}\text{N}_2\text{Zn}$	$\text{B}_{12}\text{N}_2\text{Cd}$	$\text{B}_{12}\text{N}_2\text{Be}$	B_{12}O_2	B_{12}P_2	B_{12}As_2	$\alpha\text{-B}_{12}$
cell							
a (Å)	5.2832	5.4281	5.168	5.065 (5.15) ^a	5.177 (5.25) ^b	5.229 (5.33) ^b	5.006 (5.057) ^c
α (deg)	62.0	61.1	63.2	63.3 (62.9) ^a	69.5 (69.6) ^b	70.0 (70.7) ^b	58.4 (58.06) ^c
bond length (av, Å)							
BB1	1.804	1.834	1.783	1.756	1.768	1.769	1.761
BBB1	2.083	2.118	2.058	2.027	2.042	2.042	2.033
BB2	1.712	1.721	1.724	1.673	1.724	1.742	1.683
BBB2			1.518				2.327
B–N(P,As,O)	1.515	1.524	1.547	1.472	1.888	1.949	
X(P,As)–N(P,As)	1.768	1.983			2.214	2.341	
<chgrow;lp;4q> E_g (eV)	2.3	1.4	3.0	2.1	2.7	2.9	1.7
B (GPa)	240.4	213.8	248.1	238.5	208.3	204.6	194.5
$H_{V,\text{calc}}$ (GPa)	45.7	41.5	48.7	47.1	34.7	32.9	38.6
$H_{V,\text{exp}}$ (GPa)				45 ^d			34 ^e
E_{total} (eV/cell)	−3192.7	−2762.7	−1513.3	−1812.2	−1297.6	−1283.5	−932.6

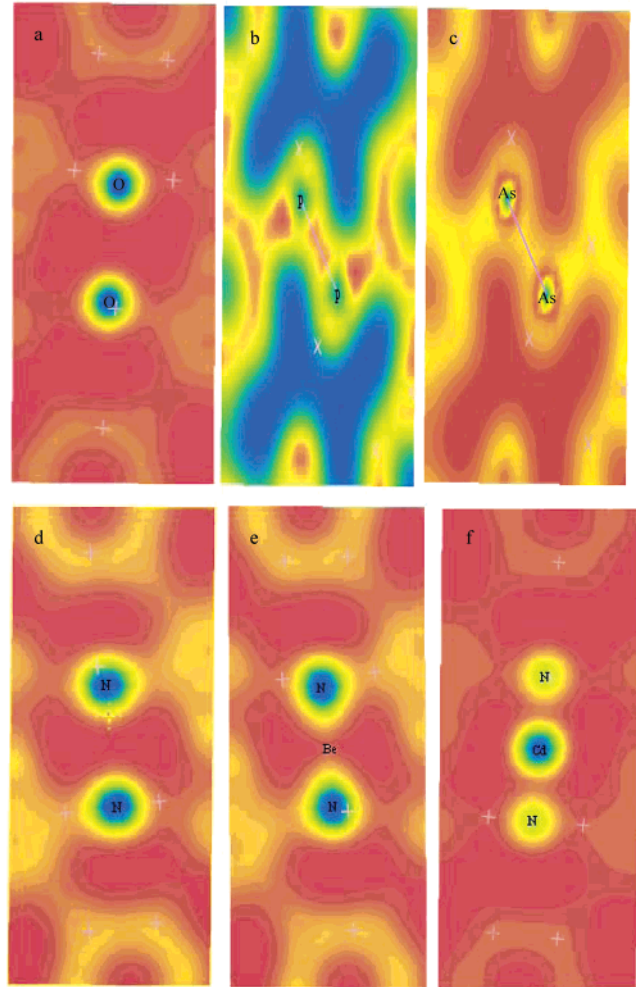
^a Experimental data from ref 22. ^b Experimental data from ref 23. ^c Experimental data from ref 15. ^d Experimental data from ref 11. ^e Experimental data from ref 24. ^f $H_{V,\text{calc}}$ and $H_{V,\text{exp}}$ are calculated and experimental microhardness, respectively.

**Figure 2.** Schematic description of Pauling bond valence of the two-atom chain of B_{12}X_2 ($\text{X} = \text{P}, \text{As}, \text{O}$), where B's are the equatorial atoms from the different icosahedra.

4) (denoted BBB2). When we add P atoms, As atoms, or O atoms to that huge hole of α -rhombohedral boron, pnictide atoms or O atoms enter the center of the dotted triangles “1” or “2” shown in Figure 1, replacing the weak three-center bond with strong covalent bonds. Six equatorial B atoms in each icosahedron bond to pnictide atoms or O atoms at the end of the two-atom chains with Pauling's bond valence of 2/3. According to Pauling's bond valence rule, the bonds of two different types of icosahedral boride two-atom chains are schematically presented in Figure 2. From Figure 2a, the bond valence of P–P (or As–As) bonds is 1. From Figure 2b, it is clear that the total valence of 2 of oxygen ion is satisfied only with bonding to three equatorial B atoms.

The current standard model is based on an ab initio approach requiring no experimental input. Calculations of the ground-state geometries on the compounds mentioned in this paper were carried out in the framework of density functional theory (DFT) with Material Studio.¹⁸ Optimizations were performed with CASTEP code. The interactions between the ions and the electrons are described by using the Ultrasoft Vanderbilt pseudopotential, and the electron–electron interaction is treated within the local density approximation (LDA) by the Ceperley–Alder exchange correlation potential. The calculations were performed using an energy cutoff of 280 eV for the plane wave basis set. The Brillouin zone is sampled on a $5 \times 5 \times 5$ Monkhorst–Pack k -point mesh. The optimization of the lattice parameters and the ion relaxation were performed iteratively until the minimum on the total energy was met. See Table 1 for optimized parameters. Figure 3 shows the charge-density contours for B_{12}O_2 (Figure 3a), B_{12}P_2 (Figure 3b), and B_{12}As_2 (Figure 3c). It is clear that the two P (As) atoms form a covalent bond and the two O atoms do not form a bond.

Based on the above analysis, B_{12}N_2 should possess N_2 chains similar to B_{12}P_2 or B_{12}As_2 . However, the N–N distance

**Figure 3.** Charge-density contours for B_{12}O_2 (a), B_{12}P_2 (b), B_{12}As_2 (c), B_{12}N_2 (d), $\text{B}_{12}\text{N}_2\text{Be}$ (e), and $\text{B}_{12}\text{N}_2\text{Cd}$ (f).

calculated by first-principles is very large, 3.035 Å, compared to the radius sum; thus N–N cannot form a bond. See Figure 3d. This results in the band structure and density of states of B_{12}N_2 not being similar to those of B_{12}P_2 or B_{12}As_2 ; see Figure 4. B_{12}P_2 and B_{12}As_2 are semiconductors, but B_{12}N_2 is metallic.

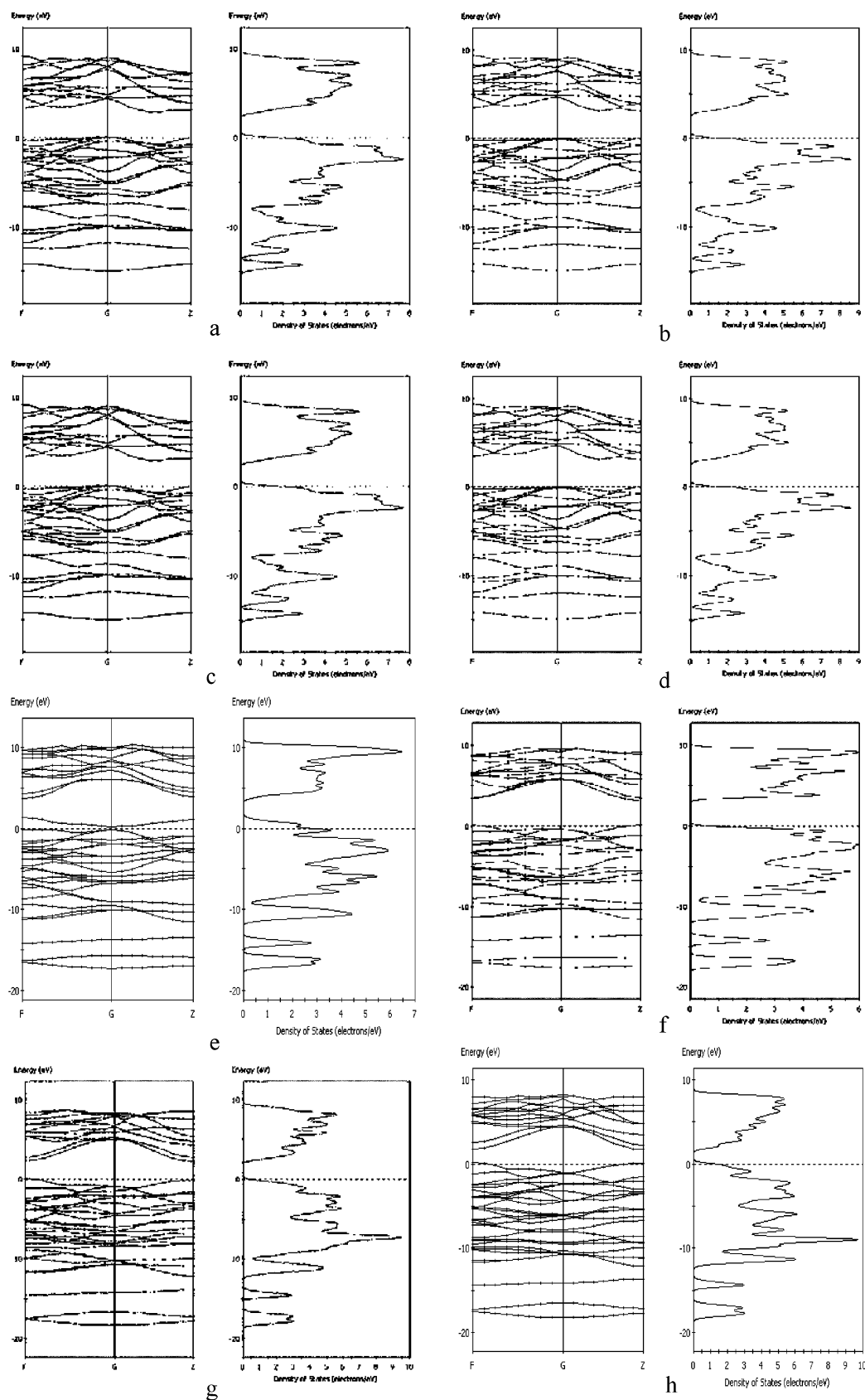


Figure 4. Band structures (left panel) and density of states (DOS) (right panel) for α - B_{12} (a), $B_{12}O_2$ (b), $B_{12}P_2$ (c), $B_{12}As_2$ (d), $B_{12}N_2$ (e), $B_{12}N_2Zn$ (f), $B_{12}N_2Cd$ (g), and $B_{12}N_2Be$ (h) calculated using the LDA.

Since the space between the two N atoms in $B_{12}N_2$ is so large, it is possible to form an N—X—N chain by adding another atom between the two N atoms. To satisfy Pauling's rule, it is necessary to select a cation carrying a valence of 2, such as Zn,

Cd, and Be. Based on this idea, $B_{12}N_2Zn$, $B_{12}N_2Cd$, and $B_{12}N_2Be$ with the boron carbide type structure are suggested as novel boron-rich compounds. $B_{12}N_2X$ (X = Zn, Cd, Be) phases can be constructed by replacing carbon atoms at (0, 0, z) in $B_{13}C_2$

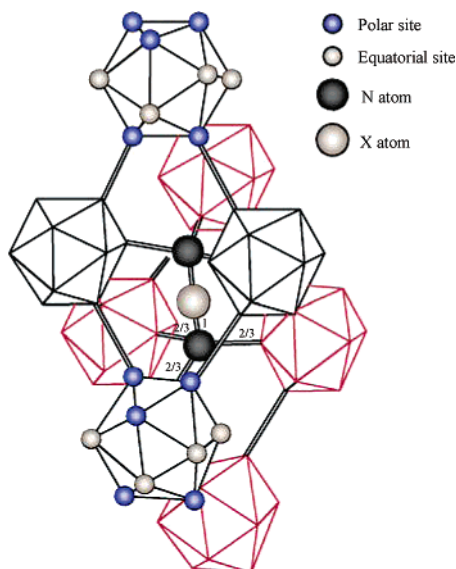


Figure 5. Schematic description of Pauling's bond valence of $B_{12}N_2X$ ($X = Zn, Cd, Be$).

with nitrogen and boron atoms at $(0, 0, 1/2)$ in $B_{13}C_2$ with Zn, Cd, or Be atoms. See Figure 5. The bonds of icosahedral boride three-atom chains of $B_{12}N_2X$ ($X = Zn, Cd, Be$) are schematically presented in Figure 5. From Figure 5, it can be seen that the three compounds proposed here satisfy Pauling's bond valence principle. We investigate the structural and electronic properties of $B_{12}N_2X$ ($X = Zn, Cd, Be$) compounds using the first-principles pseudopotential calculation mentioned above. The equilibrium structural parameters, energy gaps, bulk moduli, and total energies for $B_{12}N_2X$ ($X = Zn, Cd, Be$) phases are listed in Table 1. For comparison, those of α - B_{12} and $B_{12}X_2$ ($X = P, As, O$) calculated by first principles are also listed in Table 1. From Figure 5d, the valence band of $B_{12}N_2$ is unsaturation. When we add Be or Zn or Cd to $B_{12}N_2$, $B_{12}N_2X$ ($X = Zn, Cd, Be$) phases form and their valence bands are full occupancy; see Figure 4f–h.

In a word, if Pauling's bond valence principle can be satisfied, a stoichiometric material designed by adding atoms to boron icosahedra will be a semiconductor such as $B_{12}X_2$ ($X = P, As, O$) and $B_{12}N_2X$ ($X = Zn, Cd, Be$); otherwise it will be metallic such as $B_{12}N_2$.

According to the theory of hardness,^{17,19–21} we calculated the hardness of these boron-rich solids using the optimized parameters by first principles and list them in Table 1. The calculated microhardnesses listed in Table 1 of $B_{12}X_2$ ($X = P, As, O$) and α -boron are different from those of ref 17, because the hardness calculations in ref 17 used experimental cell parameters. By definition, "superhard" means materials whose Vickers hardness, H_V , exceeds 40 GPa.¹¹ Therefore, $B_{12}N_2X$ ($X = Zn, Cd, Be$) are superhard materials. The results shown in ref 11 suggested that $B_{12}O_2$ could be a new superhard material, surpassed in hardness only by diamond and cubic boron nitride. However, the hardness of one of the novel boron-rich materials predicted here, $B_{12}N_2Be$, is 48.7 GPa. It is greater than that of $B_{12}O_2$. Thus, $B_{12}N_2Be$ possesses greater hardness than all known boron-rich solids. On the other hand, $B_{12}N_2Be$ and $B_{12}N_2Zn$ also possess larger bulk moduli than the other boron-rich solids listed in Table 1.

According to the above method, we can design a large number of boron-rich semiconductors. Some examples are shown in Figure 6.

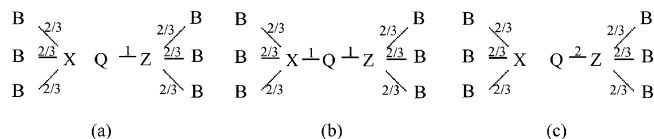


Figure 6. Schematic description of Pauling bond valence of the two-atom chain of $B_{12}XQZ$, where B's are the equatorial atoms from the different icosahedra. (a) $X = O, S$; $Q = Li, Na, \text{ or } K$; $Z = N, P, As$. (b) $X = N, P, As$; $Q = Be, Zn, Cd$; $Z = N, P, As$. (c) $X = O, S$; $Q = Be, Zn, Cd$; $Z = C$.

3. Conclusion

In conclusion, Pauling's bond valence principle is employed to design the novel boron-rich phases $B_{12}N_2X$ ($X = Zn, Cd, Be$) with the boron carbide type structure. The semiempirical model for hardness indicates that these hypothetical boron-rich phases are new superhard materials, and $B_{12}N_2Be$ is harder than all known boron-rich solids. First-principles calculations of the total energies, structures, and properties of these compounds are performed. The results show that $B_{12}N_2X$ ($X = Zn, Cd, Be$) are semiconductors with band gaps of 2.3, 1.4, and 3.0 eV, respectively. Scientifically, this might provide an example to investigate how hardness can be enhanced with microstructural complexity and chemical doping in boron-rich solids.

Acknowledgment. The authors acknowledge financial support from the National Natural Science Foundation of China (Grant 50472050) and the Program for New Century Excellent Talents in University and A Foundation for the Author of National Excellent Doctoral Dissertation of the People's Republic of China (No. 200434).

References and Notes

- (1) Riedel, R. *Handbook of ceramic hard materials*; Wiley-VCH: Weinheim, 2000.
- (2) Liu, A. Y.; Cohen, M. L. *Science* **1989**, *245*, 841.
- (3) Teter, D. M.; Hemley, R. J. *Science* **1996**, *271*, 53.
- (4) Haines, J.; Leger, J. M.; Bocquillon, G. *Annu. Rev. Mater. Res.* **2001**, *31*, 1.
- (5) Lundstron, T. In *Boron-rich solids*; Emin, D., Aselage, T. L., Switendick, A. C., Morosin, B., Eckel, C. L., Eds.; AIP: New York, 1990; p 186.
- (6) Mauri, F.; Vast, N.; Pickard, C. J. *Phys. Rev. Lett.* **2001**, *87*, 085506.
- (7) Hubert, H.; Devouard, B.; Garvie, L. A. J.; Keeffe, M. O.; Buseck, P. R.; Petuskey, W. T.; McMillan, P. F. *Nature* **1998**, *391*, 376.
- (8) Chen, M.; McCauley, J. W.; Hemker, K. J. *Science* **2003**, *299*, 1563.
- (9) Emin, D. *Phys. Today* **1987**, *40*, 55.
- (10) Domnich, V.; Gogotsi, Y. *Appl. Phys. Lett.* **2002**, *81*, 3783.
- (11) He, D.; Zhao, Y.; Daemen, L.; Qian, J.; Shen, T. D.; Zerda, T. W. *Appl. Phys. Lett.* **2002**, *81*, 643.
- (12) Li, D.; Ching, W. Y. *Phys. Rev. B* **1996**, *54*, 1451.
- (13) Shirai, K. *J. Solid State Chem.* **1997**, *133*, 215.
- (14) Cook, B. A.; Harringa, J. L.; Lewis, T. L.; Russell, A. M. *Scr. Mater.* **2000**, *42*, 597.
- (15) Greenwood, M. N.; Earnshaw, A. *Chemistry of the elements*; Pergamon Press: Oxford, 1984.
- (16) Pauling, L. *The nature of the chemical bond*; Cornell University Press: Ithaca, NY, 1960.
- (17) Gao, F. M.; Hou, L.; He, Y. H. *J. Phys. Chem. B* **2004**, *108*, 13069.
- (18) *Materials Studio*, version 2.1.5; Accelrys Inc.: 2002.
- (19) Gao, F. M.; He, J. L.; Wu, E. D.; Liu, S. M.; Yu, D. L.; Li, D. C.; Zhang, S. Y.; Tian, Y. *J. Phys. Rev. Lett.* **2003**, *91*, 015502.
- (20) Gao, F. M. *Phys. Rev. B* **2004**, *69*, 094113.
- (21) Gao, F. M.; Xu, R.; Liu, K. *Phys. Rev. B* **2005**, *71*, 052103.
- (22) Olofsson, M.; Lundstrom, T. *J. Alloys Compd.* **1997**, *257*, 91.
- (23) Emin, D. *J. Solid State Chem.* **2004**, *117*, 1619.
- (24) Szymanski, A.; Szymanski, J. M. *Hardness Estimation of Minerals Rocks and Ceramic Materials*; Elsevier: Amsterdam, 1989.