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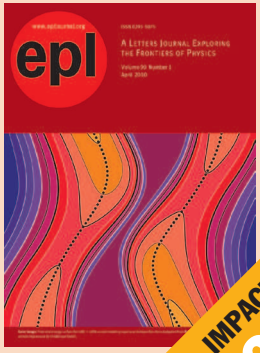

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Mechanical and electronic properties of novel tungsten nitride

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Abstract – The structure and distributions of elastic moduli of c-W_3N_4 have been investigated by first-principles calculations. The formation of c-W_3N_4 can be understood from the fact that the N atoms partially occupy the 6b (0, 1/2, 1/2) interstitial sites in pure cubic W. Young's modulus of c-W_3N_4 is found to reach a maximum along the [100] direction and a minimum along the [111] direction, and the ideal shear strength along the weakest (100)[100] slip system is about 22.5 GPa. The evidence of the bonding nature of W-N which plays an important role to form a hard material is manifested by the PDOS and Mulliken population analysis.

Introduction. – Recently, great interest for transition metal nitrides has re-emerged based on the design concept for intrinsically superhard compounds that the interaction of light elements (*e.g.*, B, C, N, and O) into the transition metal lattices forms strong covalent bonds yet keeping a high valence-electron density and bulk moduli [1,2]. Compared to early transition metals, the heavy transition metals were initially thought not to form solid nitrides for many years. Until recently, the dinitrides of Ir, Os, and Pd were successfully synthesized under high pressure and high temperature (HPHT) [3–6]. The anomalously ultra-high incompressibility of these nitrides (428 GPa for IrN_2), comparable to that of c-BN, suggests that they are potential (super)hard materials. Immediately after these pioneering studies, the rhenium nitrides with various stoichiometries (Re_2N, Re_3N, and ReN_2) [7,8] were synthesized at HPHT and some related mechanical properties were also investigated. In these Re nitrides, both Re_2N and Re_3N exhibit very high bulk moduli >400 GPa, which is higher than that of ReB_2. Moreover, ReN_2 shows the advantage over other transition metal nitrides of the relatively moderate synthesis conditions at the pressure of 7.7 GPa and temperature of 1873 K.

W is commonly referred to as refractory metal, which is close to Re and platinum-metal Os in the periodic table, it exhibits the highest melting point in the heavy transition metal family. Thus, the crystal structures and mechanical properties of tungsten nitrides have attracted much attention. In the binary W-N system, several nitrides with different stoichiometric compositions have been reported by using various techniques. However, most materials in this W-N system are in the form of thin films produced by a nonequilibrium process and are often poorly crystallized, which severely limits their use in diverse technological applications. A novel cubic W_3N_4 (c-W_3N_4) nitride was first characterized by Guenther and Schneider by using the X-ray power diffraction technique about forty years ago [9]. More recently, the well-crystallized c-W_3N_4 was successfully reproduced again by Wang *et al.* [10] using the solid-state reaction method under HPHT. Moreover, this c-W_3N_4 phase has a high measured bulk modulus of 376 GPa, which is 50% and 45% higher, respectively, than those of the previous c-Zr_3N_4 [11] and c-Hf_3N_4 [12]. Therefore, c-W_3N_4 can be potentially superhard since the incorporation of N atoms not only compensates its

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valence electron densities but also introduces the covalent bonding. Accordingly, understanding the structural, mechanical and electronic properties of c-W_3N_4 is not only of particular interest in fundamental research but also a requirement for the design of superhard materials with improved capabilities. In the present work, we have studied the structural intrinsic connections between pure W metal and c-W_3N_4 in order to investigate the incorporation of N into W lattice. Moreover, we have extended the mechanical properties and presented in detail the variations of the elastic moduli along the arbitrary directions and the ideal shear strength in the easy-slip plane. These theoretical calculations which can provide further details are highly desirable.

Computational methods. – All structure relaxations were performed using the VASP code [13] with the generalized gradient approximation (GGA) proposed by Perdew-Burke-Ernzerhof exchange-correlation functional [14]. The electron and core interactions were included by using the frozen-core all-electron projector augmented wave (PAW) potential [15] of the metal atoms including d electrons as valence states. The integration in the Brillouin zone was employed using the Monkhorst-Pack scheme [16] ($12 \times 12 \times 12$), an energy cutoff of 700 eV, and a tetrahedron method with Blöchl corrections for the energy calculation and Gaussian smearing for the stress calculations. During the geometrical optimization, all forces on atoms were converged to less than 0.001 eV/Å and the total stress tensor was reduced to the order of 0.01 GPa. Elastic constants were calculated by the strain-stress method [17] and the polycrystalline bulk modulus and shear modulus were thus derived from the Voigt-Reuss-Hill averaging scheme [18]. The quasistatic ideal strength [19] is calculated by incrementally deforming the modeled cell in the direction of the applied strain and controlling the specific strain components, and simultaneously relaxing both the other strain components, as well as the atoms inside the unit cell, at each step. The critical shear stresses along various directions were then calculated by applying shear deformations in the easy-slip plane.

Results and discussion. – For the cubic W unit cell in fig. 1(a), the lattice parameter a is 3.18 Å and each W atom is eightfold coordinated. Experiments [10] have demonstrated that the solid c-W_3N_4 (fig. 1(b)) possesses a cubic lattice of space group $Pm\bar{3}m$ (No. 221) with one formula unit in a unit cell: Two inequivalent N1 and N2 occupying the Wyckoff $1b$ (1/2, 1/2, 1/2) and $3d$ (1/2, 0, 0) sites, and W sitting at $3c$ (0, 1/2, 1/2) positions. If we consider a $1 \times 1 \times 2$ supercell for c-W_3N_4 presented in fig. 1(c), one can clearly see that this c-W_3N_4 phase consists of a fundamental building block along the c-axis: a tetragonal sublattice (dashed cell in fig. 1(c)) with lattice constants $a = b = 2.91$ Å and $c = 4.216$ Å. Strikingly, this tetragonal sublattice can be viewed as a distorted cubic W unit cell when the N atoms partially occupy the $6b$ (0, 1/2, 1/2) interstitial sites in a pure cubic W unit cell.

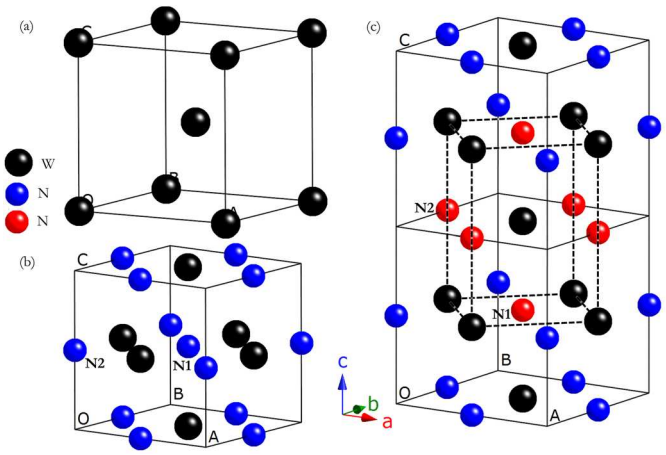

Fig. 1: (Colour on-line) Crystal structures of pure W metal (a), c-W_3N_4 (b), and $1 \times 1 \times 2$ supercell of c-W_3N_4 (c).

While by this approach, the pressure and temperature effects on the interaction of the N atoms into the W lattice for the formation of c-W_3N_4 could be understood as follows: the N atoms incorporate into the W lattice and partially locate on the $6b$ interstitial sites (which would be possible from the packing considerations) and this leads to a significantly extension of the c-lattice parameter and shrink of the $a(b)$-lattice parameter and then to the formation of a building block for c-W_3N_4: the tetragonal sublattice. The optimized equilibrium lattice constant of a_0 for c-W_3N_4 is 4.216 Å, which is in good agreement with the experimental values of 4.122 Å [9] and 4.125 Å [10]. Moreover, the total energy of c-W_3N_4 is calculated by varying the volume and these calculated E-V data are fitted to the Birch-Murnaghan equation of state (EOS) [20]. The obtained bulk modulus B_0 and its pressure derivative are 360 GPa and 4.523, which are consistent with the experimental data of 376 GPa and 4.0, confirming the accuracy and reliability of the computational procedure employed here. In order to provide some insight into the pressure behavior of c-W_3N_4, the pressure dependence of the normalized parameter a/a_0 as a function of pressure is calculated. By fitting the calculated data with the least squares method, we obtained their relationship at the temperature of 0 K as the following relation: $a/a_0 = 0.99992 - 9.04358 \times 10^{-4} P + 4.16469 \times 10^{-6} P^2$.

The elastic properties define the behavior of a solid that undergoes stress, deforms, and then recovers and returns to its original shape after stress ceases. The strain-stress method was used in calculating the elastic constants. A small finite strain was applied on the optimized structure and the atomic position was fully optimized. Then, the elastic constants were obtained from the stress of the strained structure. The obtained results are listed in table 1. For a stable cubic structure, C_{ij} should satisfy the elastic stability criteria [21]: C_{11}-$|C_{12}| > 0$, $C_{11} > 0$, $C_{44} > 0$, $C_{11} + 2C_{12} > 0$. Clearly, these calculated elastic constants completely satisfy the criteria, suggesting

Table 1: Calculated elastic constants C_{ij}, bulk modulus B_H, shear modulus G_H, and Young's modulus E_H (in units of GPa). Also shown are Poisson's ratio σ_H, the B_H/G_H ratio, and the elastic compliance constants (in units of GPa^{-1}).

c-W_3N_4	c_{11}	c_{12}	c_{44}	s_{11}	s_{12}	s_{44}	B_H	G_H	E_H	σ_H	B_H/G_H
This work	792	146	61	0.00092	0.00021	0.01639	361	128	343	0.342	2.82
Experiment [10]							376				
Theory [10]	789	144	99				368	183			

that the c-W_3N_4 is mechanically stable at ambient pressure. It should be noted that the calculated C_{11} and C_{12} agree very well with the previous theoretical values [10]. However, the value of C_{44} is smaller than that calculated by the same author. In fact, we have found that the use of different strains in steps of 0.001 from 0.001 to 0.003 in calculations leads to nearly the same C_{44} values. We are not aware of any experimental data on the elastic constants. We hope that future experimental measurements will verify all these calculated results. Using the calculated elastic constants C_{ij}, the bulk modulus B_H and shear modulus G_H for the corresponding polycrystalline aggregate are thus determined by the Voig-Reuss-Hill approximation method. In addition, Young's modulus E_H and Poisson's ratio v_H are obtained in the light of the following equations: $E_H = 9B_HG_H/(3B_H + G_H)$ and $v_H = (3B_H - 2G_H)/(6B_H + 2G_H)$. The calculated bulk modulus, shear modulus, Young's modulus, and Poisson's ratio are given in table 1. Obviously, the calculated B_H (361 GPa) is in excellent agreement with that directly obtained from the fitting of the Birch-Murnaghan EOS ($B_0 = 360$ GPa), which further demonstrates the accuracy of our elastic constants calculations. The shear modulus of a material quantifies its resistance to the shear deformation. The calculated shear modulus of c-W_3N_4 is 128 GPa, which is close to those of c-Zr_3N_4 (129 GPa) and c-Hf_3N_4 (138 GPa) [22] but larger than the theoretical value of known superhard WB_4 (104 GPa) [23]. The ratio between the bulk and the shear modulus B/G are used to predict the brittle or ductile behavior of materials. According to the Pugh criterion [24], the ductile behavior is predicted when $B/G > 1.75$, otherwise the material behaves in a brittle manner. It can be clearly seen in table 1 that the c-W_3N_4 is strongly prone to ductile with respect to the value of B_H/G_H (2.82).

A useful visualization of the elastic anisotropy can be obtained by plotting a three-dimensional picture of the dependence of Young's modulus on a direction in a crystal. For cubic materials, it is described by the following equation [25]:

$$E^{-1} = s_{11} - \beta_1(\alpha^2\beta^2 + \alpha^2\gamma^2 + \beta^2\gamma^2), \qquad (1)$$

where α, β, and γ are the direction cosines of the tensile stress direction, $\beta_1 = 2s_{11} - 2s_{12} - s_{44}$, and s_{11}, s_{22}, and s_{44}, are the elastic compliance constants which are given by Nye [26], as listed in table 1. This equation determines a three-dimensional closed surface, and the distance from the origin of the system of coordinates to this surface equals Young's modulus in a given direction. For a perfectly isotropic medium this surface would be a sphere. In fig. 2(a), it shows a well-pronounced anisotropy for c-W_3N_4 and the cross-sections of c-W_3N_4 in the bc plane are also shown in fig. 2(b) for comparison. Analytical equations for the determination of the maximum and minimum values of Young's moduli are [25] $E_{\min} = 3/(s_{11} + 2s_{12} + s44)$ and $E_{\max} = 1/s_{11}$ if $\beta_1 < 0$. The "max" and "min" subscripts should be interchanged if $\beta_1 > 0$. For c-W_3N_4, the estimated $E_{\max}$ and $E_{\min}$ values are 1084 GPa along the [100] directions and 56.4 GPa along the [111] directions for c-W_3N_4, respectively. This large difference between $E_{\max}$ and $E_{\min}$ may impose certain limitations and restrictions on possible applications of this novel nitride. Compared to the anisotropy of Young's modulus, the study of the dependence of the shear modulus G on stress direction is useful for understanding plastic deformation in c-W_3N_4. We choose a shear plane (hkl) and vary the shear stress direction [uvw] within that plane. The axis normal to the (hkl) plane is denoted as [HKL]. Thus, the shear modulus on the (hkl) shear plane with shear stress applied along the [uvw] direction can be expressed as [27]

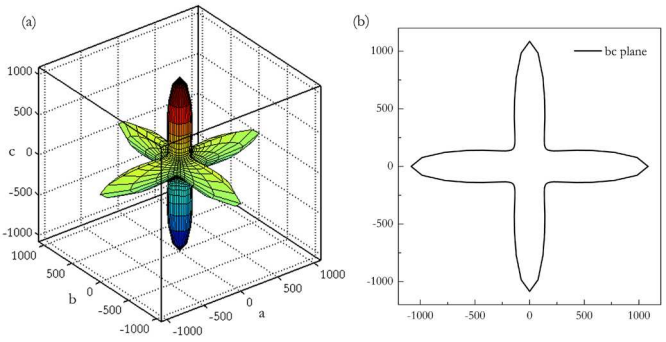

Fig. 2: (Colour on-line) Directional dependence of Young's modulus for c-W_3N_4 (a) and the projection in the bc plane (b).

$$\begin{aligned} G^{-1} &= 4s_{11}(\alpha_1^2\alpha_2^2 + \beta_1^2\beta_2^2 + \gamma_1^2\gamma_2^2) \\ &+ 8s_{12}(\alpha_1\alpha_2\beta_1\beta_2 + \beta_1\beta_2\gamma_1\gamma_2 + \alpha_1\alpha_2\gamma_1\gamma_2) \\ &+ s_{44}\left[(\beta_1\gamma_2+\beta_2\gamma_1)^2+(\alpha_1\gamma_2+\alpha_2\gamma_1)^2+(\alpha_1\beta_2+\alpha_2\beta_1)^2\right], \end{aligned} \qquad (2)$$

where α_1, β_1, γ_1, α_2, β_2, and γ_2 are the direction cosines of the [uvw] and [HKL] directions. From this equation, as plotted in fig. 3(a), the shear moduli ($G = s_{44}^{-1} = 61$ GPa) of c-W_3N_4 are independent of the shear stress direction from [100] to [010] within the (001) shear plane, of the shear stress directions from [001] to [010] within

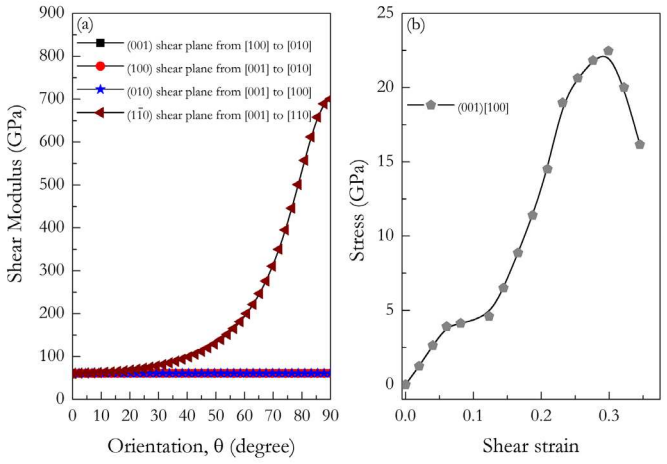

Fig. 3: (Colour on-line) Orientation dependence of the shear modulus in c-W_3N_4 (a) and ideal shear strength of c-W_3N_4 along the weakest (001) [100] direction.

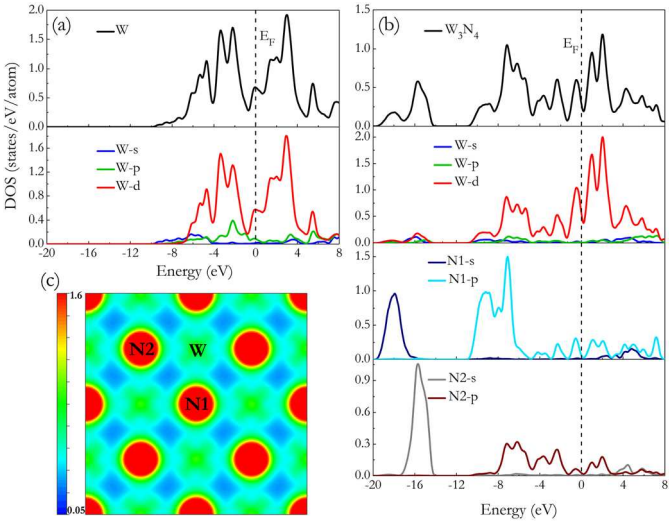

Fig. 4: (Colour on-line) Total and partial densities of states of W (a), c-W_3N_4 (b) at 0 GPa, and contours of charge density on the (001) plane (c).

the (100) shear plane, and of the shear stress directions from [001] to [100] within the (010) shear plane. For the shear plane (1$\bar{1}$0) , we rotate the shear stress from [001] to [110], then $\alpha_1 = \beta_1 = \sin\theta/\sqrt{2}$,$\gamma_1 = \cos\theta$,$\alpha_2 = \beta_2 = 1/\sqrt{2}$,$\gamma_2 = 0$, where θ is the angle between [001] and the shear stress direction. Thus, the shear modulus can be expressed as $G^{-1} = 2(s_{11} - s_{12})\sin^2\theta + s_{44}\cos^2\theta$. For c-W_3N_4 in table 1, $s_{44} > 2(s_{11} - s_{12})$, the shear modulus is the smallest along [001], which is $G = s_{44}^{-1} = 61$ GPa, and largest along [110], which is $G = [2(s_{11} - s_{12})]^{-1} = 700.3$ GPa. It can be seen from fig. 3(a) that, the shear moduli are the smallest on the (100), (001), and (010) planes and almost independent of any shear directions. This means that these principal crystal planes may be the cleavage planes of c-W_3N_4. The critical shear stress in c-W_3N_4 was then calculated by applying [100] shear deformation in the (001) easy cleavage plane, as shown in fig. 3(b). It can be seen that the ideal shear strength of c-W_3N_4 along the weakest (001)[100] slip system is about 22.5 GPa, which is higher than those of Re_2N (12.4 GPa) and Re_3N (15.5 GPa) [28]. However, the ideal shear strengths of c-W_3N_4 is much lower than those of ReB_2 (34.4 GPa) [29] and c-BN (58.3 GPa) [30], indicating much lower shear resistance or potential superhardness. In spite of its significantly higher bulk moduli, this novel tungsten nitride is much weaker than c-BN in terms of shear moduli and strengths. Thus, higher incompressibility does not necessarily guarantee higher shear resistance and hardness. Here, we roughly estimate the hardness of c-W_3N_4 based on a semiempirical approach proposed by Šimůnek [31]. The Vickers hardness of c-W_3N_4 is calculated to be 24.6 GPa, suggesting that it is potentially hard.

To gain insights into the effect of nitrogen incorporation, the electronic density of states (DOS) and bonding features of W and c-W_3N_4 are analyzed. Figure 4 shows the electronic DOS of W and W_3N_4. Both two phases show similar metallic bonding features because of finite total DOS at the Fermi level (E_F), which originate mostly from 5d electrons of W. The total DOS at the E_F, $N(E_F)$ (in states/eV/atom), which is 0.680 and 0.273 for W and W_3N_4, respectively. In addition, the Fermi level is seen to lie at a pronounced minimum in the DOS curve, a pseudogap, and this feature is suggestive of the extraordinary stability of c-W_3N_4. From the partial DOS of c-W_3N_4 phase (fig. 4(b)), we observe a strong hybridization between the N2-2p and W-5d states (from -10 to -1 eV), an evidence of covalent bonding between N2-2p and W-5d electrons. Also, the N1-2p and W-5d states (from -4 to 0 eV) strongly hybridize as well and form strong bonds. To further demonstrate this bonding nature, we show in fig. 4(c) the charge density distributions on the (001) plane. The bonding directionality is clearly revealed between W and N, a typical feature of covalent bonding. In addition, there is sizable larger bandwidth and smaller total DOS of c-W_3N_4 when compared to the total DOS of pure W in fig. 4(a). This may be due to the covalent bonding of W and N which leads to the strong overlap of W-5d and N-2p orbitals. We also performed the Mulliken population analysis of c-W_3N_4 and found a charge transfer (2.76 electrons/f.u.) from N to W, implying an ionic contribution to the W-N bonding. We thus conclude that the chemical bonding in these molybdenum borides is a complex mixture of covalent, ionic, and metallic characters. Such a conclusion was also found in other transition metal nitrides [28].

Conclusions. – To conclude, the structural, mechanical and electronic properties of recent synthesized c-W_3N_4 have been studied using first-principles calculations. Our calculated equilibrium lattice parameters, bulk modulus, and its pressure derivative are highly consistent with experimental reports. The formation of

c-W_3N_4 can be understood from the fact that the N atoms partially occupy the $6b$ (0, 1/2, 1/2) interstitial sites in pure cubic W under high pressure and high temperature. Large elastic anisotropy of Young's modulus is found between the [100] directions and [111] directions. The ideal shear strength of c-W_3N_4 along the weakest (001)[100] slip system is about 22.5 GPa, which is much lower than that of c-BN. The bonding nature in this novel nitride is a complex mixture of covalent, ionic, and metallic characters manifested by the PDOS and Mulliken population analysis.

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