Theoretical study on tetragonal transition metal dinitrides from first principles calculations

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Three new transition metal dinitrides TMN2 (TM = Ta, W, and Re) with the P4/mmb structure are investigated by the first principles calculations method based on the density functional theory. The elastic constants and phonons calculations have confirmed that these three compounds are all mechanical and dynamically stable at ambient pressure. The distributions of elastic moduli of these dinitrides have been systematically studied and the obtained results indicate that the (001) plane may be viewed as the cleavage plane for TaN2 and WN2 as well as (100) plane for ReN2. Moreover, TMN2 within this tetragonal structure are found to be ultra-incompressible and hard, among which WN2 exhibits the largest bulk modulus (389 GPa) and Vickers hardness (38.5 GPa). Density of states calculation revealed that the strong TM–N covalent bonding is the driving force for the high bulk and shear modulus as well as small Poisson’s ratio of the studied dinitrides.

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1. Introduction

Transition metal (TM) nitrides have attracted considerable attentions from both theoretical and experimental studies due to their extreme hardness and durability as well as the outstanding mechanical, electronic, magnetic and optoelectronic properties [1–3]. Most of the early transition metal mononitrides are well known hard materials. For example, TiN and CrN hard coatings are widely used in cutting tools industry [4]. Recently, great interest for transition metal nitrides has re-emerged based on the design concept for intrinsically superhard compounds that the interaction of lights elements (e.g., B, C, N, and O) into the transition metal lattices to form strong covalent bonds yet keeping a high valence-electron density and bulk moduli [5,6]. Taking advantage of high-pressure techniques, bulk TMN4 (TM = Zr, Hf) [3] with high elastic moduli and hardness has been obtained, opening new avenues for the synthesis of other TM nitrides. Subsequently, the platinum-metal (such as Pt, Ir, Os, and Pd) dinitrides were successfully synthesized under high pressure and high temperature (HPHT) [7–10]. The anomalously ultra-high incompressibility of these nitrides (428 GPa for IrN2), comparable to that of c-BN, suggests that they are potential (super)hard materials. These pioneering studies have stimulated considerable research enthusiasm for

5d TM nitrides. More recently, a hexagonal MoS2\textsuperscript{2+}-type ReN\textsubscript{2} was synthesized by metathesis reaction using X-ray diffraction under high pressure by Kawamura et al. [11]. However, a following theoretical work [12] has revealed that this MoS\textsubscript{2}–ReN\textsubscript{2} is mechanical unstable and it is actually nitrogen-vacancies in MoS\textsubscript{2}–ReN\textsubscript{2}. Strikingly, theoretical calculations for this nitrogen-vacancies phase correctly reproduce the experimental X-ray diffraction pattern. Their further structural searching identifies a possible ground state monoclinic structure and a high-pressure tetragonal phase (space group: P\textsubscript{4}/mmb, Z = 2) for ReN\textsubscript{2}. Especially, this P\textsubscript{4}/mmb-ReN\textsubscript{2} exhibits an unusual incompressibility along the c axis, close to that of diamond.

Up to now, however, TMN\textsubscript{2} (TM = Hf, Ta, and W) have not been synthesized in crystalline form when compared to other 5d TMN\textsubscript{2} (TM = Os, Ir, and Pt) compounds. Therefore, many theoretical studies [13–23] have proposed a series of hypotheses on the structures and properties of TMN\textsubscript{2} (TM = Hf, Ta, and W). Recently, HfN\textsubscript{2} and TaN\textsubscript{2} within four different structures fluoride-type, pyrite-type, P\textsubscript{6}\textsubscript{3}/mmc, and P\textsubscript{6}m\textsubscript{2} structures have been systematically studied [13–15], and these two compounds within pyrite-type structure are potential ultra-incompressible. For WN\textsubscript{2}, Wang et al. predicted [16] two types of hexagonal structures which are ultra-incompressible and are energetically superior to the previously proposed cotunnite phase [17]. Meanwhile, numerous theoretical studies have proposed different structures for ReN\textsubscript{2} [18–23], among which a tetragonal phase for ReN\textsubscript{2} suggested by Du et al. is potential superhard. Therefore, as a possible metastable phase, the
The DFT calculations have been performed within generalized gradient approximation (GGA) [24], as implemented in the Vienna ab initio simulation package (VASP) [25]. The electron and core interactions were included by using the frozen-core all-electron projector augmented wave (PAW) potential [26] of the metal atoms including d electrons as valence states. The integration in the Brillouin zone was employed using the Monkhorst–Pack scheme [27] with a grid of 0.03 Å⁻¹, an energy cutoff of 800 eV, and a tetrahedron method with Blochl corrections for the energy calculation and Gaussian smearing for the stress calculations. During the structural optimizations, all forces on atoms were converged to the order of 0.001 eV/Å, and the external stresses were reduced to be less than 0.01 GPa. The phonon calculations were carried out by using a supercell approach as implemented in the PHONOPY code [28]. Single crystal elastic constants were calculated from evaluation of stress tensor generated small strain, and the bulk modulus, shear modulus, Young’s modulus, and Poisson’s ratio were thus derived from the Voigt–Reuss–Hill approximation [29].

3. Results and discussion

The considered P4/mmbm crystal structure of TMN₂ is shown in Fig. 1. It can be seen that this P4/mmbm phase consists of a fundamental building block connected by edge along the c-axis: a tetragonal sublattice (solid line cell in Fig. 1) which can be viewed as a distorted CsCl-type structure. Table 1 lists the calculated lattice constants, equilibrium volumes, bond lengths, bulk moduli, and their pressure derivatives of TMN₂ (TM = Ta, W, and Re) along with previous theoretical values of ReN₂ [12]. The bulk moduli and their pressure derivatives are obtained by fitting pressures and cell volumes with the third-order Birch–Murnaghan equation of state (EOS) [30]. From this table, the calculated lattice parameters, equilibrium volumes and bond lengths of ReN₂ are in good agreement with previous theoretical results. However, for other compounds of TaN₂ and WN₂, there are no available experimental data and theoretical values for comparison. Therefore, the present results could provide useful information for future experimental or theoretical investigations. Moreover, as in the Birch–Murnaghan EOS treatment, we also obtained the values of equilibrium bulk moduli and their pressure derivatives for these three dinitrides presented in Table 1. It can be seen that these compounds possess a large value of bulk moduli which are comparable to those of synthesized platinum–metal dinitrides (PtN₂: 372 GPa [7], OsN₂: 358 GPa [9], IrN₂: 428 GPa [9]), but larger than previous proposed structures of TaN₂ [13,14], WN₂ [16], and ReN₂ [18–20]. Thus, one might expect their excellent ultra-incompressibility. At zero-temperature a stable crystalline structure requires all phonon frequencies to be positive. Therefore, we have performed the full phonon dispersion calculations for TMN₂ (TM = Ta, W, and Re) at 0 GPa. As shown in Fig. 2, no imaginary phonon frequency was detected in the whole Brillouin zone, indicating the dynamical stability of the TaN₂, WN₂, and ReN₂, respectively. It is important to explore the thermodynamic stability of TMN₂ with P4/mmbm structure for further experimental synthesis. The thermodynamic stability at ambient pressure with respect to decomposition is quantified in terms of the formation enthalpy, using ∆Hᵣ = H(TMN₂) − H(TM) − H(N₂). The ∆Hᵣ is the formation enthalpy, the body-centered-cubic Ta and W (space group: Im-3m), hexagonal Re (space group: P6₃/mmc), and α-phase N₂ are chosen as the reference phases. The calculated ∆Hᵣ per formula unit (f.u.) of these compounds are listed in Table 1, together with other theoretical values for WN₂. Compared to the negative formation enthalpy values of previous candidates P6₃/mmc [16], P6mm2 [16], and F21/c [22], the P4/mmbm-WN₂ is metastable with positive formation enthalpy comparable to that of P4/mmbm phase proposed by Du et al. [20]. Therefore, high temperatures are needed to synthesize this P4/mmbm structure for WN₂ in actual experiment. Results obtained by this reaction route for TaN₂ on the contrary, have demonstrated its stability against the decomposition into the mixture of Ta and N₂, suggesting that it is most likely to be synthesized at ambient pressure. In order to provide some insights into the pressure behavior of TMN₂, the pressure acting on the system as functions of lattice parameters (a/a₀ and c/c₀) and unit cell volume (V/V₀) are plotted in Fig. 3, where a₀, c₀, and V₀ are the equilibrium structural parameters at zero pressure. The structural behaviors of synthesized hexagonal Re₃N and ReN as well as c-BN under pressure were also presented in Fig. 3 for comparison. Firstly, it can be seen that the incompressibility along the c-axis is larger than that along the a-axis for each TMN₂ compound, suggesting their clear elastic anisotropy. The incompressibility of WN₂ is almost identical to that of ReN₂, but larger than that of TaN₂. Secondly, both WN₂ and ReN₂ exhibit a larger a-axis incompressibility and similar volume incompressibility when compared to recently synthesized ultra-incompressible Re₂N and ReN. Thirdly, we notice that the volume incompressibility of WN₂ and ReN₂ exceeds that of c-BN at high pressure, although c-BN has the higher bulk at zero pressure. Take WN₂ for example, by fitting obtained data with least squares meth-
od, we obtained their relationships at the temperature of 0 K as the following relations:

\[
\frac{a}{a_0} = 0.9995 - 8.36028 \times 10^{-4}P + 3.10152 \times 10^{-6}P^2
\]  

\[
\frac{c}{c_0} = 0.99992 - 7.58873 \times 10^{-4}P + 2.90318 \times 10^{-6}P^2
\]  

\[
\frac{V}{V_0} = 0.99991 - 2.41 \times 10^{-3}P + 1.00029 \times 10^{-5}P^2
\]

Table 1
Calculated equilibrium lattice constants \(a_0 (\text{Å}), c_0 (\text{Å})\), equilibrium volume \(V_0 (\text{Å}^3)\), bond length (Å), EOS fitted bulk modulus \(B_0\) (GPa), its pressure derivative \(B'_0\), and formation enthalpy \(\Delta H_f \) (eV/f.u.) for the P4/mmb-TMN₂, respectively.

<table>
<thead>
<tr>
<th>TMN₂</th>
<th>Space group</th>
<th>(a_0)</th>
<th>(b_0)</th>
<th>(c_0)</th>
<th>(V_0)</th>
<th>(d_{\text{TM-N}})</th>
<th>(d_{\text{N-N}})</th>
<th>(B_0)</th>
<th>(B'_0)</th>
<th>(\Delta H_f)</th>
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<tr>
<td>TaN₂</td>
<td>P4/mbm</td>
<td>4.403</td>
<td>2.839</td>
<td>55.041</td>
<td>2.272</td>
<td>1.410</td>
<td>343</td>
<td>4.477</td>
<td>–0.951</td>
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</tr>
<tr>
<td>WN₂</td>
<td>P4/mbm</td>
<td>4.331</td>
<td>2.761</td>
<td>51.784</td>
<td>2.221</td>
<td>1.408</td>
<td>390</td>
<td>4.590</td>
<td>0.537</td>
<td>–0.942</td>
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<tr>
<td>PW2</td>
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<td>2.934</td>
<td>7.790</td>
<td>58.07</td>
<td>2.102</td>
<td>1.405</td>
<td>378</td>
<td>4.58</td>
<td>–0.74</td>
<td></td>
</tr>
<tr>
<td>PW2</td>
<td>P4/mmm&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2.928</td>
<td>3.916</td>
<td>29.969</td>
<td>2.101</td>
<td>1.420</td>
<td>378</td>
<td>4.58</td>
<td>–0.74</td>
<td>–0.941</td>
</tr>
<tr>
<td>TW2</td>
<td>P21&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2.71</td>
<td>7.38</td>
<td>54.20</td>
<td>2.23</td>
<td>1.41</td>
<td>378</td>
<td>4.58</td>
<td>–2.67</td>
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<tr>
<td>ReN₂</td>
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<td>4.190</td>
<td>2.663</td>
<td>51.330</td>
<td>2.211</td>
<td>1.424</td>
<td>387</td>
<td>4.766</td>
<td>1.938</td>
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<tr>
<td>P&lt;sup&gt;d&lt;/sup&gt;</td>
<td>P4/mbm</td>
<td>4.390</td>
<td>2.644</td>
<td>50.955</td>
<td>2.20</td>
<td>1.453</td>
<td></td>
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<sup>a</sup> Ref. [16].  
<sup>b</sup> Ref. [20].  
<sup>c</sup> Ref. [22].  
<sup>d</sup> Ref. [12].

Fig. 2. Phonon dispersion curves of TaN₂ (a), WN₂ (b), and ReN₂ (c) within P4/mmb structure at 0 GPa.

Fig. 3. Calculated \(a\)-axis compressions \((a/a_0)\) (a), \(c\)-axis compressions \((c/c_0)\) (b), and volume compressions \((V/V_0)\) (c) as a function of pressure TMN₂, respectively.
The mechanical properties (elastic constants and elastic moduli) are essential for understanding the macroscopic mechanical properties of solids and for the design of (super)hard materials and their potential technological applications. We calculated the zero-pressure elastic constants \( C_{ij} \) of these TMN\(_2\) compounds by the strain–stress method. A small finite strain was applied on the optimized structure and the atomic positions were fully optimized. Then, the elastic constants were obtained from the stress of the strained structure. The calculated elastic constants \( C_{ij} \) are listed in Table 2, along with the previous theoretical values of the TMN\(_2\) (TM = Ta, W, and Re) [12–13, 16, 18–20, 22]. It is well known that the elastic stability is a necessary condition for a stable crystal. A tetragonal crystal has to obey the following restrictions of its elastic compliance constants \([31]\): 

\[
C_{11} > 0, \quad C_{33} > 0, \quad C_{44} > 0, \quad C_{66} > 0, \quad (C_{11} - C_{12}) > 0, \quad (C_{11} + C_{33} - 2C_{13}) > 0, \quad \text{and} \quad 2(C_{11} + C_{12}) + C_{33} + 4C_{13} > 0.
\]

As shown in Table 1, these conditions are clearly satisfied for tetragonal stability, confirming that these compounds are mechanically stable. It also can be seen that these compounds possess a remarkable value of \( C_{33} \), especially for WN\(_2\) (894 GPa), which is comparable to those of \( \text{ReB}_2 \) (838 GPa). The Poisson’s ratio \( \nu \) is \( (894 \text{ GPa}) \), which is close to that of superhard material \( \text{ReB}_2 \). For the (100) plane in Fig. 5, \( E \) is the shear modulus.

\[
E = \frac{9G(1\nu^2 + \nu)}{(3-4\nu)}
\]

where \( \nu \) is the Poisson’s ratio. The shear modulus \( G \) can be expressed as:

\[
G = C_{11} - C_{12} = \frac{\sqrt{C_{11}C_{13} - C_{12}^2}}{C_{12}}
\]

where \( \alpha, \beta, \) and \( \gamma \) are the direction cosines of \([uvw]\) direction.

Based on the calculated \( C_{ij} \), the corresponding six independent elastic compliance constants \( s_{ij} \) of the tetragonal crystal given by Srideshmukh were determined [34]. For engineering applications that make use of single crystals, it is necessary to know the values of bulk modulus, Young’s modulus, and shear modulus as a function of crystal orientation. As outlined by He et al. [35], executing the appropriate coordinate system transformations for the compliances allows the determination of the variation of Young’s moduli \( E \) and shear modulus \( G \) with crystallographic direction, \([uvw]\), for a given crystallographic plane, \((hkl)\), containing these directions, i.e., \( E_{[uvw]} \) and \( G_{[uvw]} \) are obtained. For \( P4/mmb \) crystal structure, the Young’s modulus \( E \) is expressed as:

\[
E = s_{11}(x^4 + \beta^4) + s_{12}(x^4 + 2x^2\gamma^2 + 2x^4 + \gamma^2) + s_{44}(\beta^2\gamma^2 + \gamma^2) + s_{66}\beta^2
\]

(4)

Table 2

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Phases</th>
<th>( C_{11} )</th>
<th>( C_{12} )</th>
<th>( C_{13} )</th>
<th>( C_{33} )</th>
<th>( C_{44} )</th>
<th>( C_{66} )</th>
<th>( B_0 )</th>
<th>( G_0 )</th>
<th>( E_0 )</th>
<th>( n_s )</th>
<th>( B_0/G_0 )</th>
<th>( H_s )</th>
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<td>TaN(_2)</td>
<td>( P4/mmb )</td>
<td>651</td>
<td>771</td>
<td>204</td>
<td>205</td>
<td>228</td>
<td>125</td>
<td>340</td>
<td>225</td>
<td>552</td>
<td>0.2296</td>
<td>1.51</td>
<td>26.3</td>
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<td></td>
<td>Pyrite(^a)</td>
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<td>82</td>
<td>322</td>
<td>299</td>
<td>37</td>
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<tr>
<td>( \text{Pb}_6\text{mmm} )</td>
<td>785</td>
<td>894</td>
<td>308</td>
<td>188</td>
<td>165</td>
<td>389</td>
<td>300</td>
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<td>W(_2\text{N}_2)</td>
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<td>973</td>
<td>233</td>
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<td>211</td>
<td>364</td>
<td>228</td>
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<td></td>
<td></td>
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<tr>
<td></td>
<td>( P6m\text{mm})</td>
<td>588</td>
<td>973</td>
<td>232</td>
<td>191</td>
<td>206</td>
<td>364</td>
<td></td>
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<td>( P21\text{m})</td>
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<td>( P6m\text{mm} )</td>
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<td>967</td>
<td>258</td>
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<td>374</td>
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<td></td>
<td>( \text{P6}_3\text{m} )</td>
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<td>553</td>
<td>610</td>
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\( ^a \) Ref. [11].
\( ^b \) Ref. [16].
\( ^c \) Ref. [20].
\( ^d \) Ref. [22].
\( ^e \) Ref. [12].
\( ^f \) Ref. [15].
\( ^g \) Ref. [18].
the vector normal to the \((hkl)\) shear plane. For shear plane \((001)\) with the shear stress direction rotated from \([100]\) to \([010]\), the direction cosines are \(a_1 = \cos \theta\), \(b_1 = \sin \theta\), \(c_1 = 0\), \(a_2 = \beta_2 = 0\), and \(c_2 = 1\), where \(\theta\) is the angle between the \([100]\) and the shear stress direction. By solving Eq. (5), the \(G = 1/s_{44} = C_{44}\), which means that within \((001)\) plane, the shear modulus of the TMN\(_2\) is independent.

Fig. 4. Three-dimensional surface representations of the Young’s modulus for TaN\(_2\) (a), WN\(_2\) (b), and ReN\(_2\) (c).

Fig. 5. Orientation dependence of the Young’s modulus for TaN\(_2\) (a), WN\(_2\) (b), and ReN\(_2\) (c).

Fig. 6. Orientation dependence of the Shear modulus for TaN\(_2\) (a), WN\(_2\) (b), and ReN\(_2\) (c).
of the shear stress direction. For shear plane (100) with the shear stress directions [0 r w] varying from [100] to [010], the direction cosines are $\alpha_1 = 0$, $\beta_1 = \sin \theta$, $\gamma_1 = \cos \theta$, $\alpha_2 = 1$, $\beta_2 = \gamma_2 = 0$, and $C^{-1} = s_{66} + (s_{44} - s_{66}) \cos^2 \theta$. Because $s_{44} > s_{66}$ in TaN$_2$ and WN$_2$, their shear moduli are the largest along [010] and the smallest along [001]. Contrarily, ReN$_2$ possesses a maximum of $E_{[001]}$ and a minimum of $E_{[010]}$ due to $s_{44} < s_{66}$. For shear plane (110) with the shear stress directions $[u \, v \, w]$ between [001] and [110] in Fig. 6, the variation tendencies of shear moduli are similar. From Fig. 6, it is clear that the shear moduli are the smallest on the (100) plane for TaN$_2$, (100) plane for WN$_2$, and (100) plane for ReN$_2$, respectively. This means that the (001) plane may be viewed as the cleavage plane for TaN$_2$ and WN$_2$ as well as (100) plane for ReN$_2$.

Based on the calculated elastic constants, the isotropic bulk modulus ($B_{ij}$) and shear modulus ($G_{ij}$) for the TMN$_2$ polycrystalline are calculated by the Voigt–Reuss–Hill approximation [29] in Table 2. The Young’s modulus $E_{ij}$ and Poisson's ratio $\nu_{ij}$ are obtained from the equations of $E_{ij} = 9B_{ij}G_{ij}/(3B_{ij} + 2G_{ij})$ and $\nu_{ij} = (3B_{ij} - 2G_{ij})/(6B_{ij} + 2G_{ij})$. The calculated bulk modulus of the TMN$_2$ are above 340 GPa, indicating ultra-incompressible structural nature. Strikingly, it should be noted that the calculated bulk moduli agree well with those directly obtained from the fitting of the third-order Birch–Murnaghan equation of state (EOS) (see Table 1), which further demonstrates the reliability of our elastic calculations. A material with high bulk modulus is not enough to ensure its high hardness. For the partially covalent transition metal-based materials, the shear modulus of a material quantifies its resistance to the shear deformation and is a better indicator of potential hardness. The value of Poisson’s ratio is indicative of the degree of directionality of the covalent bonding, and small Poisson's ratio indicates a strong degree of covalent bonding, which contributes to the materials’ hardness. In Table 2, the WN$_2$ is found to have the highest shear modulus (300 GPa) and lowest Poisson’s ratio (0.195), which are two important elastic properties thought to be strongly correlated to hardness. Indeed, the estimated Vickers hardness ($H_v$) for WN$_2$ is 38.5 GPa, the largest one among the studied TMN$_2$ compounds based on the empirical formula for hardness prediction proposed by Chen et al. [36]. Future synthesis of this nitride and additional properties related to this excellent mechanical property. In addition, 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 [37], the ductile behavior is predicted when $B/G > 1.75$, otherwise the material would fail in a brittle manner. It can be clearly seen in Table 2 that all these TMN$_2$ compounds are strongly prone to brittle manner.

We have also obtained other fundamental properties using above calculated mechanical quantities. The Debye temperature closely relates to many physical properties of solids, such as specific, dynamic properties, and melting temperature. At low temperature, it can be calculated from the elastic constants using the average sound velocity $\nu_m$, by the following equation [38],

$$\Theta_D = \frac{\hbar}{k} \left( \frac{3nN_A}{M} \right)^{\frac{1}{3}} \nu_m$$

(6)

where $\hbar$ is Planck’s constant, $k$ is Boltzmann’s constant, $N_A$ is Avogadro’s number, $n$ is the number of atoms per formula unit, $M$ is the molecular mass per formula unit, and $\rho$ is the density. The average sound velocity $\nu_m$ is given by

$$\nu_m = \left[ \frac{1}{3} \left( \frac{2}{\nu_t} + \frac{1}{\nu_l} \right) \right]^{-\frac{1}{2}}$$

(7)

here $\nu_t$ and $\nu_l$ are the transverse and longitudinal elastic wave velocities of the polycrystalline materials, which can be obtained using the polycrystalline bulk modulus and shear modulus from Navier’s equation [38]. The calculated Debye temperatures of these TMN$_2$ compounds increase in the following sequence: TaN$_2$ (666 K) < ReN$_2$ (697 K) < WN$_2$ (753 K), which is the same as the trend in estimated hardness of TMN$_2$ listed in Table 2. This can be naturally explained by the empirical linear relationship between hardness and Debye temperature proposed by Abrahams and Hsu [39].

To illustrate the mechanical properties on a fundamental level, the total and site projected electronic densities of states (DOS) of TMN$_2$ (TM = Ta, W, and Re) at 0 GPa were plotted in Fig. 7, where the vertical dot line is the Fermi level. Clearly, all these structures exhibit metallic behavior by evidence of the finite electronic DOS at the Fermi level ($E_F$). From the partial DOS, it reveals that the TM-5 orbital has a significant hybridization with N-2p orbital localized in the energy range from −10 eV to 0 eV, indicating the strong TM–N covalent bonding nature. Therefore, the strong covalent Ta–N bond is the main driving force for their high bulk and shear moduli as well as small Poisson’s ratio. In addition, the contribution to Fermi level is mainly due to TM-5d orbital which is the principal cause for their metalliclicity. The typical feature of the total DOS is the presence of so-called pseudogap [40], which is considered as the borderline between the bonding and antibonding states. It can be seen that the $E_F$ of is WN$_2$ and ReN$_2$ nearly lying on the pseudogap, respectively, indicating the $p$-d bonding states started to be saturated. This nearly full occupation of the bonding states enhances the stability of WN$_2$ and ReN$_2$. We also performed the Mulliken population analysis of these nitrides and found a charge transfer from TM to N, implying an ionic contribution to the TM–N bonding. We thus conclude that the chemical bonding in these molybdenum borides is a complex mixture of covalent, ionic, and metallic.

![Fig. 7. Total and partial densities of states of TaN$_2$ (a), WN$_2$ (b), and ReN$_2$ (c) at 0 GPa. The vertical dashed line is the Fermi energy.](image-url)
characters. Such a conclusion was also found in other transition metal nitrides.

4. Conclusions

In summary, by means of density functional theory calculations, we have systematically studied the structural stability, mechanical properties, electronic structure and chemical bonding of TMN₂ (TM = Ta, W, and Re) within \( P4/mbm \) structure. The elastic constants and phonons calculations show that these three compounds are all mechanical and dynamically stable. The Young’s modulus and shear modulus as a function of crystal orientation were systematically investigated. The results indicate that the (001) plane may be viewed as the cleavage plane for TaN₂ and WN₂ as well as (100) plane for ReN₂. The calculated bulk moduli and hardness suggested that these nitrides are ultra-incompressible and hard materials. The electronic densities of states analysis have demonstrated that the strong covalent TM–N bonding plays a key role in the ultra-incompressibility and hardness of the TMN₂. These findings will inevitably stimulate extensive experimental works on synthesizing these technologically important materials.

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