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# Theoretical study on tetragonal transition metal dinitrides from first principles calculations

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Three new transition metal dinitrides $TMN_2$ (TM = Ta, W, and Re) with the *P*4/*mbm* 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 $TaN_2$ and $WN_2$ as well as (100) plane for $ReN_2$. Moreover, $TMN_2$ within this tetragonal structure are found to be ultra-incompressible and hard, among which $WN_2$ 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.

## 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 TM3N4 (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 $IrN_2$), comparable to that of *c*-BN, suggests that they are potential (super)hard materials. These pioneering studies have stimulated considerable research enthusiasm for 5*d* TM nitrides. More recently, a hexagonal $MoS_2$-type $ReN_2$ 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 $MoS_2$–$ReN_2$ is mechanical unstable and it is actually nitrogen-vacancies in $MoS_2$–$ReN_2$. 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*4/*mbm*, *Z* = 2) for ReN2. Especially, this *P*4/*mbm*-$ReN_2$ exhibits an unusual incompressibility along the *c* axis, close to that of diamond.

Up to now, however, $TMN_2$ (TM = Hf, Ta, and W) have not been synthesized in crystalline form when compared to other 5*d* $TMN_2$ (TM = Os, Ir, and Pt) compounds. Therefore, many theoretical studies [13–23] have proposed a series of hypotheses on the structures and properties of $TMN_2$ (TM = Hf, Ta, and W). Recently, $HfN_2$ and $TaN_2$ within four different structures fluorite-type, pyrite-type, $P6_3/mmc$, and $P\bar{6}m2$ structures have been systematically studied [13–15], and these two compounds within pyrite-type structure are potential ultra-incompressible. For $WN_2$, 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 $ReN_2$ [18–23], among which a tetragonal phase for $ReN_2$ suggested by Du et al. is potential superhard. Therefore, as a possible metastable phase, the

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*P*4/*mbm*-$ReN_2$-type structure mentioned above can be extended by those of Hf, Ta, and W which can provide further details are highly desirable. However, the calculated phonon dispersion curves in the present work indicate that only $TaN_2$ and $WN_2$ with the *P*4/*mbm* structure are dynamically stable. Accordingly, to explore such possibilities and provide guidance for future experimental efforts, here we perform first principles density functional theory (DFT) calculations to investigate the structural stability, mechanical properties, electronic properties, and chemical bonding of $TaN_2$ and $WN_2$ in comparison with $ReN_2$. The calculated results indicate that these dinitrides are mechanically stable and exhibit excellent mechanical properties. We hope our results can stimulate further experimental research to synthesize these ultra-incompressible and potential (super)hard compounds.

## 2. Computational methods

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 Blöchl 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].

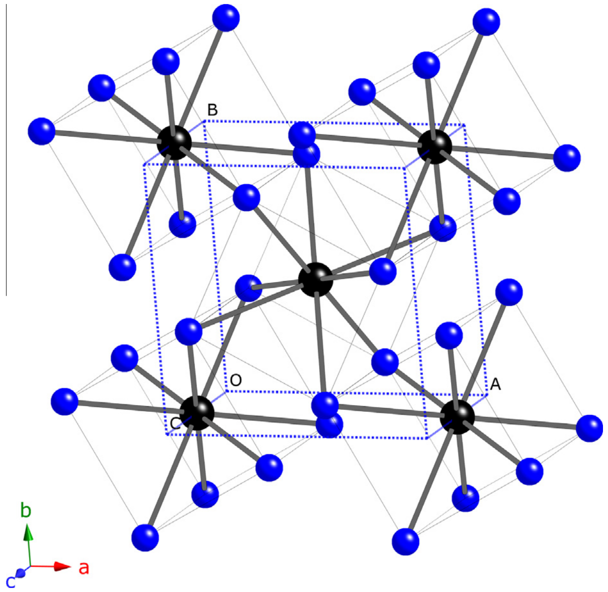

**Fig. 1.** Crystal structure of the tetragonal *P*4/*mbm* phase. The black and blue spheres represent TM and N atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

## 3. Results and discussion

The considered *P*4/*mbm* crystal structure of $TMN_2$ is shown in Fig. 1. It can be seen that this *P*4/*mbm* 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 $TMN_2$ (TM = Ta, W, and Re) along with previous theoretical values of $ReN_2$ [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 $ReN_2$ are in good agreement with previous theoretical results. However, for other compounds of $TaN_2$ and $WN_2$, there are no available experimental data and theoretical values for comparison. Therefore, the present results could provide useful information for further 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 ($PtN_2$: 372 GPa [7], $OsN_2$: 358 GPa [9], $IrN_2$: 428 GPa [9]), but larger than previous proposed structures of $TaN_2$ [13,14], $WN_2$ [16], and $ReN_2$ [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 $TMN_2$ (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 $TaN_2$, $WN_2$, and $ReN_2$, respectively. It is important to explore the thermodynamic stability of $TMN_2$ with *P*4/*mbm* structure for further experimental synthesis. The thermodynamic stability at ambient pressure with respect to decomposition is quantified in terms of the formation enthalpy, using $\Delta H_f = H_{(TMN_2)} - H_{(TM)} - H_{(N_2)}$. The $\Delta H_f$ is the formation enthalpy, the body-centered-cubic Ta and W (space group: *Im*-3*m*), hexagonal Re (space group: $P6_3/mmc$), and α-phase $N_2$ are chosen as the reference phases. The calculated $\Delta H_f$ per formula unit (f.u.) of these compounds are listed in Table 1, together with other theoretical values for $WN_2$. Compared to the negative formation enthalpy values of previous candidates $P6_3/mmc$ [16], $P\bar{6}m2$ [16], and *P*21/*c* [22], the *P*4/*mbm*-$WN_2$ is metastable with positive formation enthalpy comparable to that of *P*4/*mmm* phase proposed by Du et al. [20]. Therefore, high temperatures are needed to synthesize this *P*4/*mbm* structure for $WN_2$ in actual experiment. Results obtained by this reaction route for $TaN_2$, on the contrary, have demonstrated its stability against the decomposition into the mixture of Ta and $N_2$, suggesting that it is most likely to be synthesized at ambient pressure.

In order to provide some insights into the pressure behavior of $TMN_2$, the pressure acting on the system as functions of lattice parameters ($a/a_0$ and $c/c_0$) and unit cell volume ($V/V_0$) are plotted in Fig. 3, where $a_0$, $c_0$, and $V_0$ are the equilibrium structural parameters at zero pressure. The structural behaviors of synthesized hexagonal $Re_2N$ and $Re_3N$ 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 $TMN_2$ compound, suggesting their clear elastic anisotropy. The incompressibility of $WN_2$ is almost identical to that of $ReN_2$, but larger than that of $TaN_2$. Secondly, both $WN_2$ and $ReN_2$ exhibit a larger *a*-axis incompressibility and similar volume incompressibility when compared to recently synthesized ultra-incompressible $Re_2N$ and $Re_3N$. Thirdly, we notice that the volume incompressibility of $WN_2$ and $ReN_2$ exceeds that of *c*-BN at high pressure, although *c*-BN has the higher bulk at zero pressure. Take $WN_2$ for example, by fitting obtained data with least squares meth-