Nitrogen concentration driving the hardness of rhenium nitrides

Zhonglong Zhao, Kuo Bao, Da Li, Defang Duan, Fubo Tian, Xilian Jin, Changbo Chen, Xiaoli Huang, Bingbing Liu & Tian Cui

The structures and properties of rhenium nitrides are studied with density function based first principle method. New candidate ground states or high-pressure phases at Re:N ratios of 3 : 2, 1 : 3, and 1 : 4 are identified via a series of evolutionary structure searches. We find that the 3D polyhedral stacking with strong covalent N-N and Re-N bonding could stabilize Re nitrides to form nitrogen rich phases, meanwhile, remarkably improve the mechanical performance than that of sub-nitrides, as Re3N, Re2N, and Re3N2. By evaluating the trends of the crystal configuration, electronic structure, elastic properties, and hardness as a function of the N concentration, we proves that the N content is the key factor affecting the metallicity and hardness of Re nitrides.

The combination of electron-rich 4d and 5d transition metals (TM) with light covalent-bond forming elements (LE) like B, C, N, and O has been proved to be an effective way to design novel superhard material over the past decade1–3. The idea is that the collaboration of TM’s high electron concentration (EC) and the directional bonding formed by strong hybridizations between TM d electrons and LE p electrons can effectively withstand both elastic and plastic deformations. With this philosophy, compounds such as OsB2, ReB2, PtN2, IrN2, OsN2, and PdN2 were successfully designed. All of them are promising candidates for superhard and fracture-resistant materials with the elastic modulus comparable to diamond and c-BN. Recently, two Re sub-nitrides Re3N (SG P-6m2) and Re5N (SG P6/mmc) were synthesized by Friedrich et al.16 at moderate pressures (13–20 GPa) and temperatures (1600–2400 K). The ultra-high bulk modulus of > 400 GPa made them novel ultra-incompressible materials10–17. However, independent theoretical works by Zhang et al.18 and Zang et al.19 proved that the relatively lower ideal tensile strengths inherently limit the application of Re3N and Re5N as superhard material. This discrepancy tells that the small compressibility is not equal to high hardness20, and the high EC of Re sub-nitrides which is responsible for their low compressibility should actually go against the directional bonding. The Re:N stoichiometry may be the key to understand the competition between the EC and the directional bonding. And recent experimental and theoretical attempts to design N-rich Re nitrides are the subjects of intensive interest. Zhao et al.21 and Wang et al.22 proposed that Re mononitride forms in wurtzite-type, NbO-type, and NiAs-type structures, respectively. Besides, orthorhombic (SG Pbcn) and tetragonal (SG P4/mmm) Re dinitrides (denoted as orth-ReN2 and tet-ReN2) with high bulk and shear modulus has been predicted theoretically23–25. Recently, Kawamura et al.26 synthesized the MoS2-type ReN2 with metathesis reaction. However, the MoS2-type ReN2 with a weak bulk modulus is less stable according to the calculations of Wang et al.27, and a monoclinic structure (SG C2/m) was proposed. In addition, the hypothetical ReP4-type ReN4 with high computational hardness has also been predicted by Zhao et al.28 and Aydin et al.29.

Despite the substantial amount of works focused on Re nitrides. There are still two questions to be answered. Firstly, the multiple oxidation states of Re promise the emergence of Re-N phases at wide stoichiometries and pressures. Therefore a comprehensive study to update the Re-N phase diagram toward different Re:N ratios and pressures, especially in the N-rich side, is necessary. Secondly, the effect of the N concentration on the mechanical behavior of Re nitrides and relevant mechanism are still unclear. To address these issues, we employ a series of evolutionary structure searches to reconstruct the low-T Re-N phase diagram at moderate pressures of 0–100 GPa. New stable phases for the known Re:N ratios and new stoichiometries were updated and established. The trends of the crystal structure, electronic transition, and mechanical performance of Re nitrides as a function of N concentration are compared based on the updated full-scale Re-N phase diagram. The results show that the metallicity and hardness of Re nitrides cannot be correlated to the N content, and N-rich Re nitrides are better candidates for superhard materials due to the strong 3D covalent structural networks.
Results and discussion

The global stability of Re nitrides can be quantified by constructing the thermodynamic convex hull within considered pressures, which is defined as the average atom formation enthalpy of the most stable phases at each composition: \( \Delta H = H(Re,N_x) - xH(Re) - yH(N_2)/2 \). Any structure with the enthalpy lies on the convex hull is considered to be thermodynamically stable and synthesizable experimentally. To give a more realistic prediction, both the experimental and computational high-P (low-T) phase orders of nitrogen were adopted (the \( \zeta-N_2 \) was replaced by \( \epsilon-N_2 \) in the calculations due to its structural uncertainty). The formation energy \( E_f \) of predicted Re nitrides can be calculated in the same way, listed in Table 1. The high-pressure convex hull and pressure-composition phase diagram of Re nitrides are depicted in Figure 1 and Figure 2. We present a rich phase content of Re nitrides toward different Re:N ratios and pressures. Particularly, three stable phases denoted as \( P-6m2-Re_3N_2 \), \( \text{Imm}2-ReN_3 \), and \( Cmmm-ReN_4 \), beside the well-known \( Re_3N \), \( Re_2N \) sub-nitrides, and N-rich \( ReN_2 \), are proposed here as the complements to the Re-N phase diagram. It follows that the formation of Re nitrides, especially in the N-rich side, will be endothermic processes at absolute 0 K and 0 GPa due to their positive formation energies toward the thermodynamic summation of Re and \( \pi-N_2 \).

| Phase       | SG            | \( a \)  | \( b \)  | \( c \)  | \( V_0 \) | \( E_f \) |
|-------------|---------------|---------|---------|---------|---------|---------|
| Re          | This work     | 2.77    | 4.48    | 14.93   |         |         |
|             | Ref. 38       | 2.76    | 4.46    |         |         |         |
| Re_3N       | This work     | 2.83    | 7.16    | 49.74   | -0.03   |         |
|             | Ref. 10       | 2.78    | 7.15    |         |         |         |
|             | Ref. 18       | 2.83    | 7.19    |         |         |         |
| Re_2N       | This work     | 2.86    | 9.87    | 34.89   | 0.03    |         |
|             | Ref. 10       | 2.83    | 9.88    |         |         |         |
|             | Ref. 18       | 2.86    | 9.88    |         |         |         |
| Re_3N_2     | This work     | 2.84    | 8.30    | 57.94   | -0.03   |         |
| ReN_2       | This work     | 6.83    | 2.84    | 9.39    | 27.77   | 0.19    |
|             | Ref. 27       | 6.82    | 2.84    | 9.36    |         |         |
| ReN_3       | This work     | 5.25    | 2.81    | 4.75    | 34.97   | 0.44    |
| ReN_4       | This work     | 7.54    | 3.59    | 2.63    | 35.50   | 0.83    |

Table 1 | Space group (SG); calculated lattice parameters, \( a, b, \) and \( c(\text{Å}) \); unit cell volume \( V_0(\text{Å}^3) \); and formation energy \( E_f(\text{eV/atom}) \) of \( Re, Re_3N, Re_2N, Re_3N_2, ReN_2, \) and \( ReN_3 \) at 0 GPa. And the parameters of high-P phase \( ReN_4 \) at 50 GPa.

Figure 1 | Convex hull diagram for Re-N system. At pressures of (a) 10 GPa, (b) 40 GPa, (c) 70 GPa, and (d) 100 GPa, respectively. Solid circles represent stable phases while open circles denote metastable phases. N-rich stoichiometries are highlighted by cyan shadows.
For Re sub-nitrides, \( \text{Re}_3\text{N} \) is stable at whole considered pressures while \( \text{Re}_2\text{N} \) is thermodynamically stable only at high pressures, which is accord with the experimental results of Friedrich et al.\cite{10} and make our thermodynamic calculations reliable. In addition to the experimental sub-nitrides, our structure searches establish the ground state of new \( \text{Re}_5\text{N}_2 \) stoichiometry for the first time (denoted as \( P-6m2-\text{Re}_5\text{N}_2 \)), which is thermodynamically stable up to 40.0 GPa as shown in Figure 1 and Figure 2. For the N-rich side, structure searching confirms that the \( C2/m-\text{ReN}_2 \) proposed by Wang et al.\cite{27} is the most stable phase and can be synthesized at the pressures of above 7.4 GPa. The previous ortho-\( \text{ReN}_2 \), tetra-\( \text{ReN}_2 \), and MoS\(_2\)-type \( \text{ReN}_2 \)\cite{28} become metastable phases during the considered pressures. With further increasing the N concentration, a new stable structure (denoted as \( Imm2-\text{ReN}_3 \)) with extended Re:N ratio of 1:3 can be synthesized at wide pressures of 38.3–100 GPa (see Figure 2 (a)). And for Re tetranitrides, the proposed \( Cmmm-\text{ReN}_4 \) is stable at elevated pressures of above 68.2 GPa, which can be viewed as the limit of high N content phase of the predicted 0–100 GPa Re-N phase diagram. Note that the hypothetical Re\(_4\)-\( \text{ReN}_4 \) predicted by Zhao et al.\cite{23} and Aydin et al.\cite{27} should also be a metastable phase and can hardly be synthesized (see Figure 1 (c)). The adoption of the computational high-\( P \) phase order of nitrogen\cite{29,30} gives consistent phase diagram of Re nitrides, displayed in Figure 2 (b), except that the stable pressures of \( Imm2-\text{ReN}_3 \) and \( Cmmm-\text{ReN}_4 \) have been raised to 39.5 and 89.8 GPa, respectively.

The crystal structures of Re nitrides are schematically showed in Figure 3. The mechanical and dynamical stabilities are examined by calculating the elastic constants (see Supplementary Table S1 online) and phonon dispersions (see Supplementary Figure S1 online), all proposed phases are mechanically stable at 0 GPa with the elastic constants meet the Born-Huang stability criteria\cite{31}. Besides, the \( P-6m2-\text{Re}_5\text{N}_2 \) is dynamically stable at 0 GPa. And N-rich \( C2/m-\text{ReN}_2 \) and \( Imm2-\text{ReN}_3 \) are tested to be dynamically stable from 0 GPa to their synthetic pressures, which means that they are quenchable to the ambient condition. The \( Cmmm-\text{ReN}_4 \) is dynamically stable at high pressures (50–100 GPa). According to Figure 3, a unique structural transition induced by increasing N content can be clearly revealed. The Re-\text{Re}-\text{Re}, Re-N, and Re-Re-N-Re lamellar stacking orders of Re\(_5\)N, Re\(_4\)N, and Re\(_3\)N\(_2\) sub-nitrides has been broken and transformed into intriguing polyhedral stacking configurations as in \( C2/m-\text{ReN}_2, Imm2-\text{ReN}_3 \), and \( Cmmm-\text{ReN}_4 \). Among them, the structure of Re\(_3\)N\(_2\) is special since it can be viewed as the substitution of the isolated N with \( \text{N}_2 \) dimer in the configuration of Re\(_2\)N. This reveals that the segregation of Re layers by N bilayer can stabilize Re nitride to low energy and also weak metallicity (see the following electronic structure discussions). With this idea, an analogous structure can be built for ReN that is by substituting the N with \( \text{N}_2 \) dimer in Re\(_2\)N along the c-axes. Along with slightly stagger of the neighbouring two Re layers, it results in \( R-3m-\text{ReN} \), which is more stable than the wurztite-\( \text{ReN} \), \( \text{NbO}-\text{ReN} \), and \( \text{NiAs}-\text{ReN} \) proposed by Zhao et al.\cite{23} and Wang et al.\cite{27} (see Figure 1 (a)), and can easily be obtained by the 1:1 fixed Re:N ratio evolutionary structure searches. However, the lamellar order with a growing number of the vertical \( \text{N}_2 \) dimers destabilize Re nitride. The \( R-3m-\text{ReN} \) is metastable and will decompose into Re\(_5\)N\(_2\) and Re\(_2\)N as shown in Figure 1. Besides, the introduction of \( \text{N}_2 \) dimer can lower the crystal density and results in large volume phases. The \( PV \) works will sacrifice the enthalpies markedly, which is responsible for the instability of Re\(_3\)N\(_2\) at high pressures. The polyhedral stacking configuration can be an effective way to stable Re nitride and forms in dense N-rich phases. For \( C2/m-\text{ReN}_2 \), the stacking consists of the corner or edge shared \( \text{ReN}_2 \) decahedrons and also bonded with N-N connections according to Figure 3 (e). With an additional N into the lattice, the stacking for \( Imm2-\text{ReN}_3 \) consists of more regular \( \text{ReN}_7 \) octahedrons with the connections of the special tri-nitrogen units (see Figure 3 (f)). As to the high-pressure phase \( Cmmm-\text{ReN}_4 \), the novel \( \text{ReN}_8 \) cubic box can actually be formed due to the coordination number of Re changing from 7 to 8. The parallel ~1.40 Å N-N bonds (0 GPa) in \( C2/m-\text{ReN}_2, Imm2-\text{ReN}_3 \), and \( Cmmm-\text{ReN}_4 \) represent the typical single N-N bond lengths in PM nitrides, e.g., 1.41 Å for Pt\(_2\)N\(_2\), 1.43 Å for Os\(_2\)N\(_2\), and 1.42 Å for Ir\(_2\)N\(_2\), therefore we can draw the conclusion that N-N forms in single bond since the bond-length similarity within a related bonding scheme\cite{21}. The common polyhedral stacking configurations of N-rich Re nitrides is a prerequisite for superhard since it can avoid the direct Re-Re interactions, and the structural networks can be constructed primarily by Re-N and N-N covalent bonds. The space group, calculated equilibrium lattice parameters, and the unit cell volumes of rhenium nitrides with various stoichiometries are listed in Table 1. Our calculated lattice parameters of Re, Re\(_3\)N, Re\(_4\)N, and \( C2/m-\text{ReN}_2 \) are all in good accordance with previous studies\cite{10,23,24,27,28}.

The updated full-scale Re-N phase diagram allows us to evaluate the trend of the mechanical performance of Re nitrides as the function of N concentration, and correlate it with the structural and electronic transitions. The calculated bulk modulus (\( B \)), shear modulus (\( G \)), Young’s modulus (\( E \)), Poisson’s ratios (\( \nu \)), densities (\( \rho \)), and hardness (\( H_v \)) of Re nitrides at different N concentrations are depicted in Figure 4 and Table 2 (for comparability, the elastic data of the high-\( P \) phase \( Cmmm-\text{ReN}_4 \) in Figure 4 are achieved at 0 GPa), while the electronic density of states (DOS) are showed in Figure 5. Re nitrides have similar metallic bonding features owing to the finite DOS at the Fermi level (\( E_F \)), which originate mostly from 5d electrons of Re. According to Figure 4 (a) and (c), the high N content in the crystal can decrease the bulk modulus and densities markedly, which heralds the decrease of the incompressibility and EC of N-rich Re nitrides. This is accords with the reducing of the metallicity, i.e., the
DOS at the Fermi level ($N(E_F)$), of Re nitrides at elevated N concentrations. Here, we should note that the Imm2-ReN$_3$, with the lowest $B$ possess the $N(E_F)$ minimum of $\sim$0.11 eV/atom (see Figure 5). On the other hand, a parallel increase of shear modulus, Young's modulus, and a reduction of Poisson's ratio can be clearly revealed with increasing N contents, as shown in Figure 5 (b), (c), and (d). The unsmooth change of the $G$, $E$, and $v$ between the Re$_3$N, Re$_2$N, and Re$_3$N$_2$ sub-nitrides can be attributed to the discontinuity of the C12 and C13 elastic constants (see Supplementary Table S1 online), which relate to the Poisson effect in the hexagonal structures. According to Table 2, the calculated mean value of the $G$ and $E$ for N-rich $C2/m$-Re$_3$N$_2$, $Imm2$-ReN$_3$, and $Cmmm$-ReN$_4$ are about 46 and 86 GPa respectively higher than that of Re and sub-nitrides. In addition, the Poisson's ratios of $Imm2$-ReN$_3$ and $Cmmm$-ReN$_4$ have been dropped down from the typically delocalized metals ($-0.3$) to the level of strong directional covalent materials ($-0.2$). The reinforcement of the N-rich Re nitrides has its own origin and can be attributed to the enhanced hybridizations between N 2p and Re 5d electronic states (i.e., in the bonding states of $-5$ to $0$ eV below the Fermi level) as shown in Figure 5. Therefore, we can conclude that the primary contribution of the high N content to N-rich Re nitrides is that it facilitates more $p$ electrons involved in bonding, thus can translate the material from high PC metal strong sub-nitrides to the strong covalent N-rich nitrides with enhanced directional bonds. These results suggest that the N content is a key factor to influence the hardness of Re nitrides and the hardness of $C2/m$-Re$_3$N$_2$, $Imm2$-ReN$_3$, and $Cmmm$-ReN$_4$ should be far higher than that of Re$_3$N, Re$_2$N, and Re$_3$N$_2$ sub-nitrides.

The hardness of Re nitrides as a function of N concentration is estimated by recently proposed empirical model$^{40,45}$ with the formula $H_v = 2.0(k^2E)^{0.863} - 3.0$, as shown in Figure 4 (f). It can be seen that the high N content promote the hardness of Re nitrides according with the changes of $G$, $E$, and $v$ as discussed above. On the other hand, the strong covalency of the bonding in N-rich Re nitrides allows us to evaluate their intrinsic hardness by microscopic hardness models$^{40-42}$. Here we use the method proposed by Gao et al.$^{40}$ and its further development which includes a small metallic component of chemical bond and considering the orbital form of $s-p$ or $s-p-d$ hybrids. The hardness of the $\mu$-type particular bond in metallic and $s-p-d$ hybridized crystals is written as$^{40,42,45}$:

$$H_v^\mu(GPa) = A_0(N_n)^{1/2}(d^{1/2})^{-2.5}e^{1.191H_v^{s-d} - 32.2G_\mu^{s-d}}$$

(1)

where $A_0$ is the proportionality coefficient takes 350 and 1051 for the pure covalent N-N and polar covalent Re-N bonds, respectively. $N_n$ is the valence electron density of the bond, $d$ is the bond length. The Phillips iconicity $f_i$ of chemical bond is calculated by the Mulliken population$^{44}$. The $f_{si}$ in Equation (1) is a factor introduced to account for the metallic effect on hardness and can be calculated as $f_{si} = k_iTD_i/n_v$, where $n_v$ is the total number of valence electrons in the unit cell, $D_i$ is the density of electronic states at the Fermi level$^{44}$. The total hardness can be expressed as the average of all bond hard-nesses:

$$H_v = \left[ \prod (H_v^\mu)^n \right]^{1/\sum n_v}$$

(2)

where $n$ is the number of bond of type $\mu$ composing the actual complex crystal. The detailed bond parameters of hardness calculations can be found as Supplementary Table S2 online. The hardness of $C2/m$-Re$_3$N$_2$, $Imm2$-ReN$_3$, and $Cmmm$-ReN$_4$ at ambient condition are evaluated as 38.4 and 44.4 GPa respectively, which could be potential candidates to be superhard materials.

**Conclusion**

In summary, we have systematically explored the structures and properties of Re nitrides at wide stoichiometries and pressures with ab initio evolutionary method. We corrected the stable structure of Re$_3$N$_2$ to the phase with the Cmmm symmetry, and new stoichiometries of P-6m2-Re$_5$N$_2$ and $Imm2$-ReN$_3$ are established for possible synthesis. It is found that high-pressure can be an effective approach to stable Re nitrides. The $C2/m$-Re$_3$N$_2$, $Imm2$-ReN$_3$, and $Cmmm$-ReN$_4$ can be synthesized at pressures above 7.4, 38.3, and 68.2 GPa, respectively. And $C2/m$-Re$_3$N$_2$ and $Imm2$-ReN$_3$ are retainable to ambient condition. A good relation between the mechanical behavior and N concentration of Re nitrides was established by detailed evaluating the variations of the crystal configurations, electronic structures, elastic properties, and computational hardness. Our
results show that the high N content benefits the formation of the covalent 3D polyhedral stacking structure and can effectively avoid the weak Re-Re metal interactions, which result in the reinforcement of the Re nitrides from ultra-incompressible sub-nitrides to super-hard N-rich materials. These results are expected to stimulate the exploration and discovery of new material, and the approach of harden Re nitride by high NE content may also applicable to other TM compounds.

Methods
Evolutionary structure searches are performed with USPEX code47–49. Structure cells with ReN ratios of 3:1, 2:1, 1.5:1, 1:1, 1:1.5, 1:2, 1:2.5, 1:3, 1:4, 1:5, and 1:6

Table 2 | Calculated bulk modulus $B$ (GPa), shear modulus $G$ (GPa), Young’s modulus $E$ (GPa), Poisson’s ratio $\nu$, density $\rho$ (g/cm$^3$), and Vickers hardness $H_v$ (GPa) of Re-N system at different pressures

| Phase   | SG       | $P$  | $B$  | $G$  | $E$  | $\nu$ | $\rho$ | $H_v$ |
|---------|----------|------|------|------|------|-------|-------|-------|
| Re      | $P6_3/mmc$ | 0 GPa | 376  | 185  | 477  | 0.29  | 20.72 | 15.49 |
| Re$_2$N | $P-6m2$  | 0 GPa | 397  | 202  | 518  | 0.28  | 19.12 | 17.26 |
| Re$_3$N | $P6_3/mmc$ | 0 GPa | 399  | 189  | 490  | 0.30  | 18.40 | 14.98 |
| Re$_3$N$_2$ | $P-6m2$ | 0 GPa | 379  | 209  | 529  | 0.27  | 16.82 | 19.63 |
| ReN$_2$ | $C2/m$   | 0 GPa | 376  | 210  | 531  | 0.26  | 12.81 | 19.86 |
| ReN$_3$ | $Imm2$   | 0 GPa | 330  | 234  | 568  | 0.21  | 10.84 | 29.51 |
| ReN$_4$ | $Cmmm$   | 0 GPa | 354  | 283  | 670  | 0.18  | 10.15 | 38.72 |
| ReN$_4$ | $Cmmm$   | 50 GPa | 528  | 379  | 919  | 0.21  | 11.33 | 40.82 |
within 2 and 4 formula units (f.u.) are implemented at 0, 30, 60, and 100 GPa, respectively. To update a full-scale Re-N phase diagram, moreover, variable-composition structure predictions are also performed at 0, 50, and 100 GPa, respectively. The first generation of structures was produced randomly and the succeeding generations were obtained by applying heredity (60%), atom transmutation (10%), and lattice mutation (30%) operations. Each structure was fully relaxed to an energy minimum at different pressures with the Vienna ab initio simulation package (VASP). The projector augmented waves (PAW) method within the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) was adopted. By performing accurate convergence tests, we choose a cutoff of 520 eV for the wave function expansion into plane waves and a k-mesh of $0.03 \times 2\pi \AA^{-1}$ within the Monkhorst-Pack scheme for sample the Brillouin zone, which ensures the error bars of total energies are less than 1 meV/atom. Besides, all forces on atoms were converged to less than 1 meV/Å and the total stress tensor was reduced to the order of 0.01 GPa. Phonon curves were calculated by the direct supercell method with the forces obtained by the Hellmann-Feynman theorem. Elastic constants were calculated by the strain-stress method, while bulk modulus $B$ and Poisson's ratio $\nu$ are derived from the Voigt-Reuss-Hill averaging scheme. The theoretical Vickers hardness was estimated by using the Chen's model and the Gao's model, respectively. For the latter, the Mulliken bond population is calculated with the CASTEP code. The ultra-soft Vanderbilt pseudopotential (USPP) with PBE-GGA is chosen. The cutoff energy and k-mesh are the same as the setting in VASP calculations.

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Author Contributions

T.C. initiated the project. Z.Z. performed the first principle calculations and prepared all figures. Z.Z., K.B. and T.C. analyzed the data and wrote the manuscript text. D.L., D.D., F.T., X.J., C.C., X.H. and B.L. reviewed the manuscript.

Additional information

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