High-pressure synthesis of ultraincompressible hard rhenium nitride pernitride Re$_2$(N$_2$)(N)$_2$ stable at ambient conditions

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High-pressure synthesis in diamond anvil cells can yield unique compounds with advanced properties, but often they are either unrecoverable at ambient conditions or produced in quantity insufficient for properties characterization. Here we report the synthesis of metallic, ultraincompressible ($K_0 = 428(10)$ GPa), and very hard (nanoindentation hardness 36.7(8) GPa) rhenium nitride pernitride Re$_2$(N$_2$)(N)$_2$. Unlike known transition metals pernitrides Re$_2$(N$_2$)(N)$_2$ contains both pernitride N$_2^4^-$ and discrete N$_3^-$ anions, which explains its exceptional properties. Re$_2$(N$_2$)(N)$_2$ can be obtained via a reaction between rhenium and nitrogen in a diamond anvil cell at pressures from 40 to 90 GPa and is recoverable at ambient conditions. We develop a route to scale up its synthesis through a reaction between rhenium and ammonium azide, NH$_4$N$_3$, in a large-volume press at 33 GPa. Although metallic bonding is typically seen incompatible with intrinsic hardness, Re$_2$(N$_2$)(N)$_2$ turned to be at a threshold for superhard materials.
According to the approach formulated by Yeung et al.,
the design of novel superhard materials should be based on
the combination of a metal with high valence electron
density with the first-row main-group elements, which form short
covalent bonds to prevent dislocations. This conclusion was based
on the synthesis of hard borides, such as OsB₂⁵, ReB₂⁵–⁶, FeB₂⁶, or
WB₂⁷, whose crystal structures possess covalently bonded boron
networks. Similar to boron, nitrogen as well can form covalent
nitrogen–nitrogen bonds, but there are several factors, which
make it difficult to synthesize nitrogen-rich nitrides. The large
bond enthalpy of the triply bound N₂ molecule (941 kJ·mol⁻¹)⁸
makes this element generally unreactive. In many reactions the
activation barrier for N₂ bond breaking requires temperatures,
which are higher than the decomposition temperatures of the
target phases. MN₄ compounds with x > 1 are rarely available via
direct nitridation reactions or ammonothermal syntheses⁹,¹⁰.

Therefore, binary M-N systems are often limited to interstitial
metal-rich nitrides. Usually, they are less compressible and have
higher bulk moduli in comparison with pure metals due to the
increasing repulsion between metal and nitrogen atoms, whereas
their shear moduli are not always much different from those of
metals.

Application of pressure is one way to increase the chemical
potential of nitrogen and to stabilize nitrogen-rich phases¹¹.
Several transition metal dinitrides, PtN₂¹², PdN₃¹³, IrN₂¹⁴,
OsN₂¹⁴, TiN₂¹⁵, RhN₆¹⁶, RuN₂¹⁷, CoN₂¹⁸, and FeN₂¹⁹, containing
covalently bound dinitrogen units were recently synthesized
in laser-heated diamond anvil cells (LHDACs) via reactions
between elemental metal and nitrogen in a pressure range of
40–80 GPa. Although LHDAC is an efficient method to study
high-pressure chemical reactions, it is challenging to scale up the
synthesis. The search for suitable synthetic strategies, which
would enable an appropriate reaction to be realized in a large
volume press (LVP) instead of a LHDAC, is an important chal-
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Results

Synthesis of Re₂(N₂)(N)₂ in a laser-heated diamond anvil cell.
We have studied chemical reactions between Re and nitrogen and
other reagents, such as sodium azide NaN₃ and ammonium azide
NH₄N₃, in LHDACs in a range of 29–86 GPa at temperatures of
2000–2500 K (Table 1, Experiments #1 through #6). The reactions
products typically contained numerous single-crystalline grains of
several rhenium nitride phases (Table 1), which were identified
using synchrotron single-crystal X-ray diffraction (Supplemen-
tary Note 1, Supplementary Fig. 1, Supplementary Tables 1–3).
A direct reaction between Re and N₂ (Table 1) resulted in the
synthesis of three rhenium nitrides ReN₂, Re₂N, and ReN₀.₆, two of
which (ReN₂ and ReN₀.₆) have never been observed before.
The third phase identified in these experiments, Re₂N₆ (P6₃/mmc),
has previously been reported. After a stepwise decompression of
the sample obtained in Experiment #1 down to the ambient
pressure, all of the three phases (ReN₂, ReN₀.₆, Re₂N) were found to
remain intact even after being exposed to atmospheric oxygen
and moisture for several months. Crystal structure analysis of
ReN₀.₆ showed that it has a defect WC structure type (space
group P6₃m2) (for details on ReN₀.₆ see Supplementary Note 2,
Supplementary Figs. 2 and 3, Supplementary Table 4).

Analysis of the crystal structure of Re₂N₂ revealed its unusual
characteristic. Figure 1 shows the crystal structure of Re₂N₂,
which is built of distorted Re₇N₁ capped trigonal prisms (Fig. 1d)
and contains both N–N units (dumbbells) (Fig. 1f) and discrete N
atoms (N₂) (Fig. 1e) in an atomic ratio 1:1. The N₁–N₁ dumbbells are located in a trigonal antiprism formed by Re atoms
(Fig. 1f), while discrete N₂ atoms have a tetrahedral coordination
by Re (Fig. 1e). The N₁–N₁ bond length (d₁₁,₁₁ = 1.412(16) Å at
ambient conditions) suggests that the N₂ unit should be
considered as a pernitride anion N₂⁴⁻. Therefore, ReN₂ is a
rhenium nitride pernitride and its crystal-chemical formula is
Re⁺V₂[N-N]⁻₁[N⁺−][N⁻][N⁻][N⁻][N⁻]. In the following discussion we
interchangeably use both empirical formula ReN₂ and crystal-
chemical formula for this compound.

Compressibility of Re₂(N₂)(N)₂. The compressibility of Re₂N₂
was measured on the sample #2 (Table 1), which was synthesized
at 49 GPa, then decompressed down to ambient conditions, and
re-loaded into another DAC with a neon pressure-transmitting
medium, which provides much better hydrostaticity of the sample
environment than nitrogen. The sample was first characterized
using single-crystal XRD at ambient conditions. On compression,

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Table 1 Summary of syntheses

| Experiment | Technique | Reagents | Pressure (GPa) | Temperature (K) | Products                  |
|------------|-----------|----------|---------------|----------------|--------------------------|
| 1          | LHDAC     | Re + N₂  | 42            | 2200 (300)     | ReN₂ + Re₂N + ReN₀.₆    |
| 2          | LHDAC     | Re + N₂  | 49            | 2200 (300)     | ReN₂ + ReN₂             |
| 3          | LHDAC     | Re + N₂  | 71            | 2500 (300)     | ReN₂ + ReN₆             |
| 4          | LHDAC     | Re + N₂  | 86            | 2400 (300)     | ReN₂ + ReN₆             |
| 5          | LHDAC     | Re + Na₃ | 29            | 2000 (300)     | NaReN₂ + ReN₂           |
| 6          | LHDAC     | Re + NH₄N₂| 43            | 2273 (100)     | ReN₂ + ReN₀.₆ + Re₂N    |
| 7          | LVP       | Re + NH₄N₂| 33            |                | ReN₂ + Re₂N             |
the lattice parameters were extracted from the powder XRD data (Fig. 2a, b; Supplementary Note 3, Supplementary Figs. 4-6; Supplementary Table 5). The pressure-volume dependence was described using the third-order Birch–Murnaghan equation of state with the following fit parameters: $V_0 = 107.21(4) \, \text{Å}^3$, $K_0 = 428(10) \, \text{GPa}$, $K'_0 = 1.6(5)$. Figure 2c shows a plot of correlated values of $K_0$ and $K'$ to different confidence levels. Thus, $K_0$ of ReN$_2$ is larger than that of any compound in the Re-N system and is comparable to that of diamond ($K_0 = 440 \, \text{GPa}$) and IrN$_2$ ($K_0 = 428(12) \, \text{GPa}$). Among very incompressible pernitrides of transition metals, ReN$_2$ is the only compound, in which the metal atom has oxidation state $+\text{IV}$. The enhancement of the bulk modulus of ReN$_2$ in comparison to OsN$_2$, PtN$_2$, and TiN$_2$ is therefore in agreement with the general trend, that the bulk modulus of a compound increases with an increase of the product of formal charges of anions and cations$^{19,27}$.

**Search for solid nitrogen precursor.** More detail characterization of physical properties of ReN$_2$, such as hardness, electrical conductivity, etc. require a sample to be at least a few tens of microns in size that is much larger than can be synthesized in a LHDAC. The large volume press technique enables the synthesis of such a sample, but precludes from using N$_2$ as a reagent. First, the amount of nitrogen, which can be sealed in a capsule along with Re, is insufficient for the desired reaction yield; second, unavoidable deformation of the capsule upon compression may potentially lead to the loss of nitrogen. Therefore, a solid source of nitrogen had to be found and we tested sodium and ammonium azides, NaN$_3$ and NH$_4$N$_3$, as potential precursors in LHDACs (Experiments #5, #6, Table 1) (for a discussion regarding the choice of the solid reagents see Supplementary Note 4). The experiment with NaN$_3$ (Experiment #5) did not result in the synthesis of ReN$_2$. The major product of the reaction was NaReN$_2$ (Supplementary Fig. 7), whose lattice parameters turned out to be very close to those reported for m-ReN$_2$ by Kawamura et al.$^{23}$, that might suggest that the material described in ref. $^{23}$ as rhenium nitride indeed could be a different compound (for a related discussion see Supplementary Note 4). The experiment in LHDAC with NH$_4$N$_3$ as a source of nitrogen resulted in the synthesis of ReN$_2$ among other products (Experiment #6, Table 1).

**Synthesis of Re$_2$(N$_2$)(N)$_2$ in a large volume press.** Based on results of this experiment in DAC, we explored a possibility to scale up the synthesis of ReN$_2$ in a multianvil LVP at 33 GPa and 2273 K via a reaction between rhenium and ammonium azide (Experiment #7, Supplementary Note 5, Supplementary Fig. 8). The product of the reaction was a mixture of Re$_2$N$_2$ and ReN$_2$. Each phase was separated (Supplementary Fig. 9) and characterized using single-crystal X-ray diffraction. A phase-pure polycrystalline sample of ReN$_2$ ($70 \times 60 \times 50 \, \mu\text{m}^3$), which was synthesized in the LVP, was used for nanoindentation hardness and electrical resistance measurements (Supplementary Fig. 10). Nanoindentation was performed using a nanoindenter equipped with Berkovich diamond tip and featuring continuous stiffness measurement capabilities. The average hardness and Young’s modulus measured between 200 and 400 nm depths are 36.7(8) GPa and 493(14) GPa, respectively (Fig. 2e, Table 2). The hardness approaching 40 GPa, a threshold for superhard materials, and extreme stiffness comparable with diamond makes...
mechanical properties of ReN$_2$ exceptional in the row of metal nitrides. Due to the directional N–N bonding, the hardness of ReN$_2$ is higher than that of known interstitial transition metal nitrides ($\delta$-NbN ~20 GPa, HfN ~19.5 GPa, ZrN ~17.4 GPa$^{28}$, CrN ~17 GPa$^1$ etc.). Most transition metal pernitrides MN$_2$ that are metastable at ambient conditions are expected to be very hard compounds too, however they were never obtained in a quantity sufficient for the hardness measurements$^{29,30}$.

The electrical resistance of ReN$_2$ as a function of temperature was measured at ambient pressure on a sample with the dimensions of about 70 × 60 × 50 $\mu$m$^3$. The results of the measurements in the range of 150 K to 400 K are shown in Fig. 2.
Theoretical calculations. To confirm the experimentally observed peculiarities of ReN$_2$ and to gain deeper insights into the mechanical and electronic properties of this compound, we performed theoretical calculations based on the density functional theory. First, we considered the crystal structure of ReN$_2$. We carried out the full structure optimization for the compound at ambient pressure and found that calculations and experiment are in very close agreement (Supplementary Table 2). Calculated elastic constants for ReN$_2$ (Table 3) fulfill the mechanical stability conditions$^{31}$, and calculated phonon dispersion relations (Fig. 3a) show only real frequencies confirming its dynamic stability. Theoretically calculated N1–N1 vibrational frequency form a localized band giving rise to a peak of the phonon density of states at ~1031 cm$^{-1}$. This vibrational behavior is similar to other pernitrides$^{32,13,32}$. The metallic nature of the material confirmed by our calculations of the electronic density of states (DOS) (Fig. 3c). Calculated vibrational and electronic properties of N1–N1 unit confirm that it is a pernitrane N$_2^4$-. On the contrary, electronic and vibrational properties of N2 atoms (Fig. 3a, c) are quite distinct from those of N1, providing strong support to the experimental observation of the crystal chemistry of ReN$_2$, which is unique for transition metals pernitrides.

Table 2 Mean hardness and Young’s modulus of ReN$_2$ measured by nanoindentation in the 200–400 nm depth range

| Material | Hardness (GPa) | Young’s modulus (GPa) |
|----------|---------------|-----------------------|
| ReN$_2$  | 36.7 (8)      | 493 (14)              |
| Re       | 10.9 (6)      | 424 (12)              |

Note: The error estimate corresponds to the standard deviation between 16 different locations.

Discussion

The unique chemistry of the compound is essential for understanding its superior mechanical properties. The bulk modulus, calculated theoretically using Voigt-Reuss-Hill approximation (413.5 GPa)$^{33}$ is in a good agreement with the experiment (428 (10) GPa), confirming that ReN$_2$ can be characterized as highly incompressible material. At the same time, the value of the Poisson coefficient is close to 0.25, and relatively high ratio between share and bulk elastic moduli indicates substantial degree of covalence in ReN$_2$ chemical bonding. A direct calculation of the charge density map (Fig. 3b) confirms the expectation. One sees a formation of covalent bonds between two N1 atoms. It is of single bond character with very high degree of electron localization (Fig. 3d) typical for a pernitrane anion N$_2^4$-. In other transition metal pernitrides$^{34}$ and incompressible N$_2^4$- is supposed to contribute to very low compressibility of the materials. The covalent bond between Re and N2 atoms is formed by substantially less localized electrons (compare Fig. 3b and 3d). Indeed, measured temperature dependence of the electrical resistance (Fig. 2f) and the estimated resistivity (~4 x 10$^{-6}$ Ω·m–16 x 10$^{-6}$ Ω·m in a temperature range 150–400 K) are in agreement with the theoretical conclusion and the description of ReN$_2$ as a metal. The formation of the covalent bonds between Re and N2 atoms indicates strong hybridization between the electronic states of the atoms. The calculated electronic DOS (Fig. 3c) shows the presence of the pseudogap between occupied, predominantly bonding states of Re and unoccupied non-bonding and anti-bonding states. According to Jhi et al.$^{35}$, such features optimize electronic contribution to hardness enhancement in transition-metal carbonitrides, which can also explain very high hardness of ReN$_2$. Thus, the formation of strong covalent bond between Re and N2 atoms, a unique feature of the material synthesized in this work in comparison with known transition metal pernitrides, appears to be essential for its spectacular mechanical and electronic properties. To summarize, in the present work we have synthesized a transition metal nitride ReN$_2$ (Re$^{+}$(V$^{II}$(N$^{-}$II))$_2$(N$^{-}$III))$_2$ with the unique crystal structure and outstanding properties. The structure with Re atoms in the high oxidation state +V features both discrete nitride and pernitrone ions. A combination of the high electron density of the transition metal with interstitial nitride anions and covalently bound pernitride units makes this compound ultraincompressible and extremely hard at the same time. The developed method for scaling up the synthesis of ReN$_2$ in a LVP using ammonium azide as a nitrogen precursor can be applied for producing nitrides of other transition metals. We demonstrated the complete route for materials development from screening experiments in diamond anvil cells to the synthesis of samples large enough for physical property measurements. It is not only our results per se that are important, but the fact that the development and synthesis of the new material was realized contrary to the established concepts and should encourage further theoretical and experimental works in the field.

Methods

Synthesis of Re-N phases in laser-heated diamond anvil cells. In all synthesis experiments a rhenium powder (Sigma Aldrich, 99.995%) was loaded into the sample chamber of a BIX90 diamond anvil cell (Boehler–Almax anvils, 250-μm gap). In four experiments the chamber was filled with nitrogen at 1.5 kbar that served as a pressure-transmitting medium and as a reagent. In two experiments, the chamber was filled either with ammonium azide NH$_4$N$_3$ or with sodium azide NaN$_3$. Pressure was determined using the equation of state of rhenium$^{36–38}$. The compressed sample was heated using the double-sided laser-heating system installed at the Bayerisches Geoinstitut (BGI), University of Bayreuth, Germany. Successful syntheses were performed at 40, 42, 49, 71, and 86 GPa at temperatures of 2200–2500 K (Table 1).

Synthesis of Re-N phases in the large-volume press. High-pressure synthesis was performed using a Kawase-type multi-anvil apparatus IRIS15, installed at the BGI$^{49}$. The NH$_4$N$_3$ sample (0.5 mm thickness, 0.8 mm in diameter) was sandwiched between two layers of Re powder (0.1 mm thick, 0.8 mm in diameter) and between two tubes of dense alumina in a Re capsule, which also acted as a heater. The capsule was placed in a 5 wt% Cr$_2$O$_3$-doped MgO octahedron with a 5.7 mm edge that was used as the pressure medium. The assembly scheme is given in the Supplementary Fig. 8. Eight tungsten carbide cubes with 1.5 mm truncation edge lengths were used to generate high pressures. The assembly was pressurized at ambient temperature to 33 GPa, following the calibration given by Ishii et al.$^{50}$ and then heated to ~2273(100) K within 5 min and immediately quenched after the target temperature was reached. The assembly was then decompressed during 16 h.

Synthesis of NH$_4$N$_3$. Ammonium azide, NH$_4$N$_3$, was obtained by the metathesis reaction between NH$_4$NO$_3$ (2.666 g, 33 mmol, Sigma-Aldrich, 99.0%) and NaN$_3$ (2.165 g, 33 mmol, Acros Organics, Geel, Belgium, 99%) in a Schlenk tube. By heating from room temperature to 170°C in a glass oven and annealing for 7.5 h at 170°C and then for 12 h at 185°C, NH$_4$N$_3$ precipitated at the cold end of the tube separated from NaN$_3$, which remained at the hot end during the reaction$^{40}$.

Compressibility measurements. For the compressibility measurements the sample synthesized at 49 GPa and 2200 K (Experiment #2) was quenched down to ambient pressure and re-loaded into another diamond anvil cell. The sample chamber was then filled with Ne that served as a pressure-transmitting medium. A powder of gold (Sigma Aldrich, 99.99%) was placed into the sample chamber along with the sample and used as a pressure standard$^{41}$. The sample was compressed up to ~45 GPa in 13 steps. At each pressure point we have collected powder X-ray diffraction data.
Synchrotron X-ray diffraction. High-pressure single-crystal and powder synchrotron X-ray diffraction studies of the reaction products were performed at the beamlines P02.2 (DESY, Hamburg, Germany)\textsuperscript{42}, ID15B (ESRF, Grenoble, France), and 13-IDD GSECARS beamline (APS, Argonne, USA). The following beamline setups were used: P02.2: $\lambda = 0.29$ Å, beam size $\approx 2 \times 2$ μm$^2$, Perkin Elmer XRD 1621 detector; ID15B: $\lambda = 0.41$, beam size $\approx 10 \times 10$ μm$^2$, Mar555 flat panel detector; GSECARS: $\lambda = 0.2952$ Å, beam size $\approx 3 \times 3$ μm$^2$, Pilatus CdTe 1 M detector. For the single-crystal XRD measurements samples were rotated around a vertical $\omega$-axis in a range $\pm 38^\circ$. The diffraction images were collected with an angular step $\Delta \omega = 0.5^\circ$ and an exposure time of 1 s/frame. For analysis of the single-crystal diffraction data we used the CrysAlisPro software package. To calibrate an instrumental model in the $\omega$-axis in a range $\pm 20^\circ$ the same calibration crystal was used at all the beamlines.

Powder diffraction measurements were performed either without sample rotation (still images) or upon continuous rotation in the range $\pm 20^\circ$. The images were integrated to powder patterns with Dioptas software\textsuperscript{43}. Le Bail fits of the diffraction patterns were performed with the TOPAS6 software.

In-house X-ray diffraction. Ambient-pressure single-crystal XRD datasets were collected with a high-brilliance Rigaku diffractometer (Ag Ka radiation) equipped with Osmic focusing X-ray optics and Bruker Apex CCD detector in the BGI. The images were integrated to powder patterns with Dioptas software\textsuperscript{43}. Le-Bail fits of the diffraction patterns were performed with the TOPAS6 software. Note: Elastic constants $C_{ij}$ (GPa), bulk modulus $B$ (GPa), shear modulus $G$ (GPa), Young’s modulus $E$ (GPa), and Poisson’s ratio ($\nu$) were calculated with the TOPAS6 software.

Temperature-dependent resistance measurements. The resistance of the sample was measured by four-probe method passing a constant DC 90 mA current through the sample and measuring both current and voltage drop across the sample. Temperature was measured using the $\kappa$-type thermocouple.

**Table 3 Calculated elastic properties of $\text{ReN}_2$**

| $C_{11}$ (GPa) | $C_{12}$ (GPa) | $C_{13}$ (GPa) | $C_{15}$ (GPa) | $C_{22}$ (GPa) | $C_{23}$ (GPa) | $C_{25}$ (GPa) | $C_{33}$ (GPa) | $C_{35}$ (GPa) |
|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 869.51         | 230.73         | 261.47         | 51.01          | 748.93         | 251.83         | 26.67          | 648.06         | 16.61          |
| $C_{44}$ (GPa) | $C_{66}$ (GPa) | $C_{55}$ (GPa) | $\lambda$     | $B$            | $G$            | $E$            | $\nu$          |
| 257.43         | 35.91          | 299.94         | 413.5          | 262            | 26.67          | 650            | 0.24           |

Note: Elastic constants $C_{ij}$ (GPa), bulk modulus $B$ (GPa), shear modulus $G$ (GPa), Young’s modulus $E$ (GPa), and Poisson’s ratio ($\nu$) were calculated with the TOPAS6 software.

**Fig. 3 Phonon and electronic structure calculations for $\text{ReN}_2$.** Calculated phonon dispersion relations (a), charge density map (b), densities of states (c), and electron localization function (d) for $\text{ReN}_2$ at ambient conditions.
Theoretical calculations. The ab initio electronic structure calculations of ReN₂ (12 atoms), ReN (2 atoms), and ReN₂ (2×3×2 supercell) were performed using the all electron projector-augmented-wave (PAW) method as implemented in the VASP code. Among the tested exchange-correlation potentials (PBE54, PBEsol55, AM056) the PBEsol approximation has resulted into the best agreement between the derived experimental and theoretical equation of state. Convergence has been obtained with 700 eV energy cutoff for the plane wave basis and a (18×10×14) Monkhorst–Pack k-points type sampling of the Brillouin zone for ReN₂. Gaussian smearing technique was chosen with smearing of 0.05 eV. The convergence criterion for the electronic subsystem has been chosen to be equal to 10⁻⁷ eV for two subsequent iterations, and the ionic relaxation loop within the conjugated gradient method was stopped when forces became of the order of 10⁻³ eV/Å. The elastic tensor Cijk has been calculated from the total energy applying (−+) 1% and 2% lattice distortions. The Born mechanical stability conditions have been verified using the elastic constants. The phonon calculations have been performed within quasiharmonic approximation at temperature T = 0 K using the finite displacement approach implemented in PHONOPY software57. Converged phonon dispersion relations have been achieved using a (3×3×3) Monkhorst–Pack k-point sampling.

Data availability
The data that support the findings of this study are available from the corresponding author upon reasonable request. CSD-1897795 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from FIZ Karlsruhe via www.ccdc.cam.ac.uk/structures. The source data underlying Fig. 2a–f, and Supplementary Figs. 2 a–h are provided as a Source Data file. Single-crystal X-ray diffraction dataset for rhenium nitride (experiment #3 at 3.5 GPa) has been deposited to Figshare (https://figshare.com/) with the accession link https://doi.org/10.6084/m9.figshare.801852.

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References
1. Yeung, M. T., Mohammadi, R. & Kaner, R. B. Ultraincompressible, superhard materials. Annu. Rev. Mater. Res. 46, 465–485 (2016).
2. Cumberland, R. W. et al. Osmium diboride, an ultra-incompressible, hard material. J. Am. Chem. Soc. 127, 7264–7265 (2005).
3. Qin, J. et al. Is rhenium diboride a superhard material? Adv. Mater. 20, 4780–4783 (2008).
4. Dubrovinskaia, N., Dubrovinsky, L. & Solozhenko, V. L. Comment on 'synthesis of ultra-incompressible superhard rhenium diboride at ambient pressure'. Science 318, 1350 (2007).
5. Chung, H.-Y. H.-Y. et al. Synthesis of ultra-incompressible superhard rhenium diboride at ambient pressure. Science 316, 436–439 (2007).
6. Gou, H. et al. Discovery of a superhard iron tetraboride superconductor. Phys. Rev. Lett. 111, 157002 (2013).
7. Mohammad, R. et al. Tungsten tetraboride, an inexpensive superhard material. Proc. Natl Acad. Sci. USA 108, 10958–10962 (2011).
8. Andersen, T., Haugen, H. K. & Hotop, H. Binding energies in atomic negative binding. Phys. Rev. B 75, 041403 (2007).
9. Prescher, C. & Prakapenka, V. B. DIOPTAS: a program for reduction of two-dimensional X-ray diffraction data and data exploration. High. Press. Res. 35, 223–230 (2015).
10. Sheldrick, G. M. SHELXT−Integrated space-group and crystal-structure determination. Acta Crystallogr. Sect. A Found. Adv. 71, 3–8 (2015).
11. Prescher, C. & Prakapenka, V. B. DIOPTAS: a program for reduction of two-dimensional X-ray diffraction data and data exploration. High. Press. Res. 35, 223–230 (2015).
12. Sheldrick, G. M. SHELXT−Integrated space-group and crystal-structure determination. Acta Crystallogr. Sect. A Found. Adv. 71, 3–8 (2015).
13. Sheldrick, G. M. SHELXT−Integrated space-group and crystal-structure determination. Acta Crystallogr. Sect. A Found. Adv. 71, 3–8 (2015).
14. Sheldrick, G. M. SHELXT−Integrated space-group and crystal-structure determination. Acta Crystallogr. Sect. A Found. Adv. 71, 3–8 (2015).
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Author contributions

M.B., L.D., and N.D. designed the research, M.B., L.D., N.D., I.A.A. wrote the paper. M.B., L.D., S.C., T.F., G.A., Y.B.P., E.G., M.H., and A.P. H.-P.L. performed X-ray diffraction experiments, M.B. analyzed the X-ray diffraction data. F.T., A.V.P., I.A. performed theoretical calculations, H.F., M.B., T.K., S.V., W.S. performed synthesis in the large volume press and the synthesis of precursors. B.M. and P.F. performed nanodentation measurements. L.D. performed electrical resistance measurements. All authors contributed to the discussion of the results.

Additional information

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