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https://doi.org/10.1002/anie.201805152

Original publication available at:
https://doi.org/10.1002/anie.201805152

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High-pressure synthesis of a nitrogen-rich inclusion compound ReN₈·ₓN₂ with conjugated polymeric nitrogen chains

Maxim Bykov[a]*, Elena Bykova[b], Egor Koemets[b], Timofey Fedotenko[a], Georgios Aprilis[c], Konstantin Glazyrin[b], Hanns-Peter Liermann[b], Alena V. Ponomareva[d], Johan Tidholm[e], Ferenc Tasnádi[e], Igor A. Abrikosov[e], Natalia Dubrovinskaia[c], Leonid Dubrovinsky[a]

Abstract: A novel nitrogen-rich compound ReNₓN₂ was synthesized in a direct reaction between rhenium and nitrogen at high pressure and high temperature in a laser-heated diamond anvil cell. Single-crystal X-ray diffraction revealed the crystal structure, which is based on the ReNₓ framework having rectangular-shaped channels, which accommodate nitrogen molecules. Thus, despite the very high synthesis pressure, exceeding 100 GPa, ReNₓN₂ is an inclusion compound. The amount of trapped nitrogen (x) depends on the synthesis conditions. The polydiazenediyl chains [-N=N-]∞, which constitute the framework, have not been previously observed in any compound. Ab-initio calculations carried out for ReNₓN₂ provide strong support to the experimental results and conclusions.

Rhenium-nitrogen compounds are widely studied due to their promising mechanical properties, such as high or ultra-high hardness and low-compressibility.[1] Early experimental works by Hahn and Konrad[2] have shown that some rhenium nitrides (ReNₓ) can be synthesized at ambient pressure as the direct result of the high-temperature chemical reaction between NH₃ and ReCl₃ and NH₃. These nitrides have the highest nitrogen content equal to 0.43 (x ≤ 0.43). An increase of the nitrogen content in nitrides may substantially raise their stiffness[3] and hardness due to emerging covalent N-N bonds.[4] Therefore, much effort in both experimental and theoretical research has been invested into the search for nitrogen-rich rhenium-nitrogen compounds.

The emergence of the laser-heated diamond anvil cell (DAC) technique together with the development of dedicated stations at the third-generation synchrotron facilities have opened new, high-pressure routes for the synthesis of rhenium nitrides. Friedrich et al.[5] synthesized two novel compounds: Re₁₋₂N at 13 GPa and 1700 K (P=6m2, a = 2.781(1), c = 7.152(4) Å), and Re₁₋₄N at 20(2) GPa and ~2000 K (Pbca, a = 2.83(5), c = 9.88(1) Å). Both of the compounds have exceptionally large bulk moduli exceeding 400 GPa.[1]

Recently, Kawamura et al.[6] have obtained ReN₂ in the solid-state high-pressure reaction between ReCl₅ and Li₃N[4] and claimed it to have the MoS₂ structure type based on structure refinements using Rietveld method for powder X-ray diffraction (XRD) data. These results were put in doubt by Wang et al.,[7] who suggested that ReN₂ should have monoclinic C2/m symmetry and transform to the tetragonal P4/mmm phase above 130 GPa. In theoretical works, ReN₂ with pyrite[8,9] Co₃S₂[8] and NbSe₂[7,10] fluorite,[8,9] NbSe₂[7,10] and many other structure types with P4/mmm,[11] P4₂/mmm,[12] P4/mmbm[13] P-6m2[7,10] Cmcm,[10] Pbcn,[14] C2/m[9] and Pmmm[12] symmetries were considered, but have not been confirmed experimentally.

Hitherto, ReNₓ with the orthorhombic symmetry Amm2[12] is a compound with the highest nitrogen content known for the Re-N system. It was synthesized in the form of thin films by reactive magnetron sputtering.[15] There are a number of theoretically predicted nitrogen-rich compounds, which can have similar (ReNₓ (lmm2)[16]) or even higher nitrogen content, ReN₂ (Pbca[16,17], Cmcm[17]). Nitrogen-rich compounds in metal-nitrogen systems are considered as potentially high-energy density materials.[16-21]

Obviously great interest in the Re-N system calls for more systematic investigations, which could provide unambiguous structural characterization of novel Re-N phases. Although, there are several prominent examples of the synergy between powder XRD and ab-initio structure prediction algorithms,[22,23] an independent self-consistent method is required for building a reference basis for further theoretical and experimental works. In comparison to currently, most abundant high-pressure powder XRD studies, single-crystal XRD in diamond anvil cells allows not only an unequivocal structure solution, but also gives information about the chemical composition of the products of the chemical reactions occurring in laser heated DACs. In this study we used this advantage. We have synthesized a novel nitrogen-rich compound ReNₓN₂ in a laser-heated DAC and characterized its crystal structure using high-pressure single-crystal X-ray diffraction. Our experiment is complemented with theoretical analysis of the discovered compounds in the framework of density functional theory.

ReNₓN₂ resulted from a direct chemical reaction between rhenium and nitrogen at high pressure and high temperature. We conducted two independent experiments in a diamond anvil cell, in which a mixture of a Re powder and N₂ was first pressurized (to 105 GPa and 123 GPa), and then laser heated (to 2300(200) K and 2700(200) K), in one and another experiment, respectively. Nitrogen served simultaneously as a reagent and a pressure-transmitting medium (see Experimental Section for details). Although the initial reagents were powders, the chemical reaction led to the formation of numerous good-
quality single-crystal domains of the new compound, so that the
diffraction data from the quenched material could be treated
using well-established methods of the single-crystal data
analysis.\textsuperscript{[24–27]} Further, regarding the structure solution and
refinement, we will refer to the best-quality dataset collected at
\(~134\) GPa on the sample first synthesized at \(123\) GPa and
\(2700(200)\) K and then further pressurized.

Indexing revealed a body-centered orthorhombic unit cell with the
lattice parameters \(a = 3.4475(7),\ b = 6.491(11),\) and
\(c = 6.048(3)\) Å, and the symmetry \textit{Immm} (Table \(1\)). Initial
structure solution suggested the chemical formula \(\text{ReN}_8\) (Figure
1) and the structure, in which Re atoms occupy the 2\(a\) (0,0,0)
site, and nitrogen atoms \(\text{N1} – \text{the site} 16o\ (0.320(3), 0.178(3),
0.1874(16))\). Each Re atom is a member of two mutually
perpendicular almost planar \(\text{ReN}_8\) spirocycles, laying in the
planes (011) and (0-11) (Figure 1 a-c). Thus, eight nitrogen
atoms, which coordinate each Re atom, form a slightly distorted
cube. Nitrogen atoms are connected to each other forming
infinite zigzag chains running along the \(a\)-axis. Re and N1 atoms
form a framework containing square-shaped channels along the
\(a\)-axis with the side length of \(\sim 4.76\) Å (Figure 1a). The size of the
voids is sufficiently large to accommodate nitrogen molecules.
Indeed, we indeed could detect a residual electron density (6.3
e\(Å^2\)) in the channels, which allows placing another nitrogen
atom \(\text{N2}\) at the partially occupied site 4\(f\) (\(x,\frac{1}{2},0\)). The refined \(\text{N2-}
\text{N2}\) distance of 1.1(1) Å corresponds to the triple \(\equiv\) bond. We
could refine the structure at \(134\) GPa with the resultant chemical
composition \(\text{ReN}_8\cdot0.7(2)\text{N}_2\). It should be noticed that due to the
presence of heavy Re atoms and unavoidable XRD data
incompleteness imposed by design of DAC experiments, there is
a considerable uncertainty in the refined occupancy of the
trapped \(\text{N}_2\) molecule.

Additionally, we have performed \textit{ab initio} calculations
(see Experimental Section for details), which are in good
agreement with our experimental results. In particular, the
crystal structure, and the unit cell parameters of \(\text{ReN}_8\cdot\text{xN}_2\) were
very well reproduced (Table \(1\)). Simulations of the different
occupancies for the nitrogen molecules in the channels have
shown that the \(\text{ReN}_8\) framework becomes unstable and heavily
distorted on compression, if the channels are empty. Only those
frameworks, in which more than a half of the \(\text{N2}\) positions are
occupied, correspond to the experimentally determined structure
and the unit cell volume (see also discussion below).

\begin{table}[h]
\centering
\caption{Selected experimental and theoretical crystal structure
details of \(\text{ReN}_8\cdot\text{xN}_2\).}
\begin{tabular}{ll}
\hline
\textbf{Experiment:} & \\
\hline
Chemical formula & \(\text{ReN}_8\cdot0.7(2)\text{N}_2\) \\
Pressure, GPa & 134 \\
Space group & \textit{Immm} \\
a, b, c, Å & 3.4475(7), 6.491(11), 6.048(3) \\
\(V, Å^3\) & 135.4(3) \\
\(Z\) & 2 \\
No. of measured / independent reflections & 356, 165 \\
\(R_{int}\) & 0.0516 \\
Final R indexes [I>=2σ(I)] & \(R_1 = 0.0681, wR_2 = 0.1607\) \\
Final R indexes [all data] & \(R_1 = 0.0748, wR_2 = 0.1693\) \\
No. of parameters & 11 \\
\hline
\end{tabular}
\end{table}

\begin{table}[h]
\centering
\caption{Selected experimental and theoretical crystal structure
details of \(\text{ReN}_8\cdot\text{xN}_2\).}
\begin{tabular}{ll}
\hline
\textbf{Calculations:} & \\
\hline
Pressure, GPa & 126 \\
a, b, c, Å & 3.488, 6.465, 6.07 \\
\(V, Å^3\) & 135.34 \\
Re & (0,0,0) \\
\(U_{iso}(\text{Re})\) & 0.0176(7) \\
\(U_{iso}(\text{N1})\) & 0.0163(17) \\
\(U_{iso}(\text{N2})\) & 0.033(15) \\
Occupancy (\(\text{N2}\)) & 0.7(2) \\
\hline
\end{tabular}
\end{table}

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**Figure 1.** (a) Crystal structure of \(\text{ReN}_8\cdot\text{xN}_2\) at \(134\) GPa. Re and N1 atoms form a framework with rectangular-shaped channels, which accommodate N2 atoms. Blue and grey balls represent nitrogen and rhenium atoms, respectively. (b) Fragment of the crystal structure showing the coordination of Re atoms. Here only Re and N1 atoms are shown. (c) atoms in the lattice plane (0 1 -1). Out-of-plane atoms are not shown.
Figure 2. (a) Scheme of the polydiazenediyl [-N=N-]∞ chain. (b) Coordination of Re atoms by nitrogen atoms of one polydiazenediyl chain. (c) Calculated charge density maps for nitrogen chains in the (011) plane. (d) Nitrogen molecules in the (001) plane in ReN₈·N₂. (e) Calculated electronic density of states for ReN₈·N₂ (V = 135.3 Å³). (f) Calculated phonon dispersions for ReN₈·N₂.

Figure 3. Calculated (open symbols) and experimental (filled symbols) pressure dependence of the unit cell volume of ReN₈·xN₂.

Geometry of the nitrogen chains and interatomic distances provide us information about the bonding scheme in this compound. All N1 atoms have planar triangular coordination suggesting their sp² hybridization. The N1-N1 distances have lengths of 1.24(2) and 1.30(4) Å, which are intermediate between expected double and single-bonded N-N units at this pressure.[20,28]

Nitrogen chains in ReN₈·xN₂ are, therefore in accord with the description as polydiazenediyl [-N=N-]∞, which can be derived from the molecular nitrogen N≡N monomer and, to a certain extent, is a nitrogen analogue of polyacetylene[29] and polythiazyl (SN)ₓ[30] (Figure 2a).

Coordination geometry of the ReN₈ network recalls metal tetrazadiene complexes with planar MN₄ metallacycles.[31] Such compounds are successfully stabilized at ambient conditions by substituting hydrogen atoms of tetrazadiene with organic groups, while neither tetrazadiene itself nor its organic derivatives have ever been isolated. In the classical approach, the ligands can be generated in situ from organic azides or diazonium cations, and, following the discovery of Fe(MeNNNNMe)(CO)₃ by Doedens,[32] an extensive range of transition metal tetrazadiene complexes have been synthesized.[31] There are several ways how a single tetraazadiene group can coordinate a metal atom: η⁴; N-1,N-4-bridging; and N-1,N-4 metallocyclic, which is the most common.[31] Due to the delocalized π systems in such complexes, derivatives of tetrazadiene are non-innocent ligands with two canonical forms: tetrazene-1,4-diyl (M(n+2)+/RN-–N=N–N–R) and tetrazadiene (Mⁿ+/RN=N–N=NR). The distinction between these two forms is usually made based on the crystallographic information about the N-N bond lengths. Similarly, two ways of coordination exist for ReN₈·xN₂ (I and II in Figure 2b). The main difference between them is, in fact, cis- or trans-configuration of the polydiazenediyl chains. For the cis-form (I), the N₁-N₁ distances are expected to be longer than the N₁-N₂ and N₂-N₃ distances (see Figure 2b for the notation of N atoms). For compounds in the trans-form (II), the reverse is expected, i.e., the N₁-N₂ distances should be shorter. In ReN₈·xN₂, N₁-N₁ and N₂-N₃ distances are slightly shorter than N₁-N₂ (1.25(2) vs 1.30(3) Å). The difference is not considerable because of the conjugation within the nitrogen chain with a preference for the form I. The calculated charge density maps (Figure 2c) also show that there is only a very slight increase in
the electron density between N₂-N₂, N₃-N₃ compared to N₂-N₈ bonds, therefore, the bonding picture could be adequately described by the scheme III (Figure 2b). In the ionic consideration, each Re atom gives four out of its seven valence electrons to four N₄ units. Thus, each N₂ unit accommodates 2 electrons and has 22 valence electrons in total: four N-N α bond pairs (8e), four dative N---Re bonds (8e), and six π-delocalized electrons with an effective N-N bond order of 1.25. Re, therefore, should have a formal oxidation state +4. Delocalized π-system should give rise to the metallic conductivity of ReN₈·xN₂, and this conclusion is also supported by theoretical calculations (Figure 2e). Metallic nature of the compound makes Raman spectroscopy, which is often employed for the analysis of N-N bonding in nitrides, not useful here.

To the best of our knowledge, ReN₈·xN₂ is the first synthetic compound, which contains polydiazenediyil chains. Chains of the similar type were recently predicted in CaN₄[33] (η¹–coordination together with metalacyclic one), MgN₄[34], HfN₁₀[35], and in some hydrogen-nitrogen compounds[36]. Interestingly, the structure of HfN₁₀ as predicted[35] is similar to the crystal structure of ReN₈·xN₂. Recently we reported a novel compound FeN₄ containing polymeric nitrogen chains of a different type. These chains consist of both sp² and sp³ – hybridized nitrogen atoms forming catena-poly[tetraz-1-ene-1,4-diyl] chains.[37]

Next, we have also studied the compressional behavior of ReN₈·xN₂, which was first synthesized at 106 GPa (synthesis #1), and then gradually decompressed by releasing pressure in the diamond anvil cell. X-ray diffraction was measured at a few pressure points down to 22.5 GPa. Because of a substantial deterioration of the crystal quality below 90 GPa, we did not perform crystal structure refinements, but indexed the diffraction patterns and obtained the unit cell parameters. The pressure dependence of the unit cell volume of ReN₈·xN₂ (synthesis #1) could be described by the third-order Birch-Murnaghan equation of state with V₀ = 179.9 Å³, K₁ = 286(16) GPa, K₁' = 2.7(2). We could not preserve the sample below 22.5 GPa. However, potentially this compound could be recovered at ambient pressure. This argument is predicted by the calculated phonon dispersion (Figure 2f), which show dynamical stability of ReN₈·xN₂ for the entire pressure range (from volume 138 Å³ to 180 Å³).

It should be mentioned that for ReN₈·xN₂ synthesized at 123 GPa (synthesis #2), the unit cell volumes are systematically larger than those of ReN₈·xN₂ synthesized in experiment #1 (Figure 3a). This might be related to the different amount of nitrogen trapped in the channels. Indeed, the results of theoretical calculations (Figure 3b) show that the unit cell volume increases with the increase of the amount of nitrogen molecules inside the channels. Interestingly, the quantity of trapped nitrogen may also influence the mechanism of compression of ReN₈·xN₂. According to the theory (Figure 4), under compression, the channels, which are fully occupied, maintain their rectangular shape, but they tend to collapse with the negative linear compressibility of the b-axis, if the amount of N₂ is too small (Figure 4).

In summary, in this work we have synthesized a novel rhenium-nitrogen compound, in which the amount of nitrogen is highest in the Re-N system. Along with metal polyazides[38], ReN₈·xN₂ belongs to inorganic compounds with the highest nitrogen content known so far. The synthesis of ReN₈·xN₂ is a unique example of a formation of a complex porous framework in a direct reaction between two elements, in which one of the reagents plays, in addition, a role of a guest molecule essential for the stability of the synthesized compound. These results contribute to the exploration of large variety of polymeric nitrogen forms and of the role of the binding metal in chemical bonding between nitrogen atoms. Full understanding of these phenomena definitely require further joint systematic efforts from the theoretical and experimental communities.

**Experimental Section**

**Synthesis**

We have performed two series of experiments. In both of them a powder of Re was placed inside a 60 µm hole in a Re gasket, preindented to the thickness of about 22 µm. The sample chamber was loaded with nitrogen, which served as a pressure-transmitting medium. We used BX90 diamond anvil cells equipped with Boehler-Almax type diamonds (culet diameter of 120 µm). The first sample was compressed up to ~105 GPa and laser-heated up to 2300(200) K (synthesis #1), while the second sample was compressed up to ~123 GPa and then laser-heated up to 2700(150) K (synthesis #2).

**X-ray diffraction studies**

The reaction products were studied by means of single-crystal X-ray diffraction on the synchrotron beamline P02.2 at DESY, Hamburg, Germany (λ ~ 0.29 Å, Perkin Elmer XRD1621 flat panel detector).[39] At each pressure step, we collected the X-ray diffraction images upon continuous rotation of the crystal from ~20° to +20° ω. At selected pressure points, we collected the data with a narrow 0.5° scanning step in the range from ~38° to ~38° ω. We determined pressure using the equations of state of Re.[40] Diffraction data analysis (peak search, unit cell finding, data integration, frame scaling etc.) was performed with CrysAlis software. Detailed information about the treatment of the multigrain dataset is provided in the supplementary information. The crystal structures were solved and refined against single-crystal diffraction data using computer programs JANA2006[41] and OLEX2.[42] Further details of the crystal structure investigation(s) may be obtained from FIZ Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, on quoting the deposition number CSD-434024).

**Calculations**

The ab-initio calculations were performed using the supercell technique and all electron projector-augmented-wave (PAW) method[43] as implemented in the VASP code.[44–46] We used the generalized gradient approximation with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional.[47] The simulations of ReN₈·xN₂ properties were carried out using 22-atoms (x = 0 and 1), 42-atoms (x = 3/4) and 64-atoms periodic (x = 5/6) cells. The sampling for Brillouin zone integrations is performed using the Gamma scheme with 11x11x11, 6x12x12 and 4x12x12 k-point grids for x = 0 (and 1), x = 1/3, x = 5/6, respectively. The energy cutoff for the plane waves included in the expansion of wave functions was set to 700 eV. The convergence criterion for the electronic subsystem was chosen to be equal to 10⁻⁶ eV for two subsequent iterations, and the ionic relaxation loop within the conjugated gradient method was stopped when forces became of the
order of $10^2$ eV/Å. The 0 K harmonic phonon calculations were done using the finite displacement approach implemented into the PHONOPY[48]. Converged phonon dispersions were achieved using a (3x3x3) supercell with 297 atoms and 5x5x5 Monkhorst-Pack[49] k-point sampling.

Acknowledgements


COMMUNICATION

Maxim Bykov*, Elena Bykova, Egor Koemets, Timofey Fedotenko, Georgios Aprilis, Konstantin Glazyrin, Hanns-Peter Liermann, Alena V. Ponomareva, Johan Tidholm, Ferenc Tasnádi, Igor A. Abrikosov, Natalia Dubrovinskaia, Leonid Dubrovinsky

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