High-pressure synthesis of a nitrogen-rich inclusion compound $\text{ReN}_8 \cdot x\text{N}_2$ with conjugated polymeric nitrogen chains

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Abstract: A novel nitrogen-rich compound, $\text{ReN}_8 \cdot x\text{N}_2$, was synthesized via 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 that the crystal structure, which is based on the ReN_8 framework, has rectangular-shaped channels that accommodate nitrogen molecules. Thus, despite a very high synthesis pressure, exceeding 100 GPa, $\text{ReN}_8 \cdot x\text{N}_2$ is an inclusion compound. The amount of trapped nitrogen (x) depends on the synthesis conditions. The polydiazenediyl chains $[-\text{N}=\text{N}-]_\infty$, which constitute the framework, have not been previously observed in any compound. *Ab initio* calculations on $\text{ReN}_8 \cdot x\text{N}_2$ provide strong support for 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 (ReN_x) can be synthesized at ambient pressure as the direct result of the high-temperature chemical reaction between NH_4ReO_4 or ReCl_3 and NH_3 . These nitrides have the highest nitrogen content, at 0.43 ($x \leq 0.43$). An increase of the nitrogen content in nitrides may substantially raise their stiffness and hardness due to emerging covalent N-N bonds.^[3] Therefore, much effort in experimental and theoretical research has been invested in 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.*^[1] synthesized two novel compounds:

Re_3N at 13 GPa and 1700 K ($P\text{-}6m2$, $a = 2.78(1)$, $c = 7.152(4)$ Å), and Re_2N at 20(2) GPa and ~2000 K ($P6_3/mmc$, $a = 2.83(5)$, $c = 9.88(1)$ Å). Both of these compounds have exceptionally large bulk moduli exceeding 400 GPa.^[1]

Recently, Kawamura *et al.*^[4] obtained ReN_2 in the solid-state high-pressure reaction between ReCl_5 and Li_3N ,^[4] and claimed it to have the MoS_2 structure type based on structure refinements using the Rietveld method for powder X-ray diffraction (XRD) data. These results were put in doubt by Wang *et al.*,^[5] who suggested that ReN_2 should have monoclinic $C2/m$ symmetry and transform to the tetragonal $P4/mbm$ phase above 130 GPa. In theoretical works, ReN_2 with pyrite,^[6,7] CoS_2 ,^[8] fluorite,^[6,9] NbSe_2 ,^[7,10] and many other structure types with $P4/mmm$,^[11] $P4_2/mnm$,^[12] $P4/mbm$,^[13] $P\text{-}6m2$,^[7,10] $Cmcm$,^[10] $Pbcn$,^[14] $C2/m$,^[3] and $Pmmm$ ^[12] symmetries were considered, but have not been confirmed experimentally.

Hitherto, ReN_3 with the orthorhombic symmetry $Ama2$ has the highest known nitrogen content 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, that can have similar (ReN_3 ($Im\bar{m}2$)^[3]) or even higher nitrogen content, ReN_4 ($Pbca$,^[16,17] $Cmmm$)^[17]. Nitrogen-rich compounds in metal-nitrogen systems are considered potential high-energy density materials.^[18–21]

The 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 to build a reference basis for further theoretical and experimental works. In contrast to most abundant high-pressure *powder* XRD studies, single-crystal XRD in diamond anvil cells allows not only an unequivocal structure solution but also provides 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 synthesized a novel nitrogen-rich compound, $\text{ReN}_8 \cdot x\text{N}_2$, 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.

$\text{ReN}_8 \cdot x\text{N}_2$ 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 N_2 was first pressurized (to 105 GPa or 123 GPa), and then laser heated (to 2300(200) K or 2700(200) K, 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

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methods of single-crystal data analysis.^[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.

Figure 1. (a) Crystal structure of ReN₈·xN₂ 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.

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 *Immm* (Table 1). The initial structure solution suggested the chemical formula ReN₈ (Figure 1) and a structure in which Re atoms occupy the $2a$ (0,0,0) site and nitrogen atoms N1 occupy the site $16o$ (-0.320(3), 0.178(3), 0.1874(16)). Each Re atom is a member of two mutually perpendicular almost planar ReN₈ spirocycles, lying in the planes (011) and (0-11) (Figures 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 a side length of ~4.76 Å (Figure 1a). The size of the voids is sufficiently large to accommodate nitrogen molecules. Indeed, we could detect a residual electron density ($6.3 \text{ e}/\text{\AA}^3$) in the channels, which allows placing another nitrogen atom N2 at the partially occupied site $4f$ ($x, \frac{1}{2}, 0$). The refined N2-N2 distance of 1.1(1) Å corresponds to the triple N≡N bond. We could refine the structure at 134 GPa with the resultant chemical composition ReN₈·0.7(2)N₂. Due to the presence of heavy Re atoms and unavoidable XRD data incompleteness imposed by the design of DAC experiments, there is considerable uncertainty in the

refined occupancy of the trapped N₂ molecule. However, the presence of N₂ molecules in the voids is supported by Raman spectroscopy data (Supporting Information, Figure 4).

Additionally, we performed *ab initio* calculations (see Experimental Section for details), that are in good agreement with our experimental results. In particular, the crystal structure and unit cell parameters of ReN₈·xN₂ were very well reproduced (Table 1). Simulations of the different occupancies for the nitrogen molecules in the channels have shown that the ReN₈ framework becomes unstable and heavily distorted upon compression if the channels are empty. Only those frameworks in which more than a half of the N2 positions are occupied correspond to the experimentally determined structure and the unit cell volume (see also discussion below).

Table 1. Selected experimental and theoretical crystal structure details of ReN₈·xN₂.

Experiment:	
Chemical formula	ReN ₈ ·0.7(2)N ₂
Pressure, GPa	134
Space group	<i>Immm</i>
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 \geq 2\sigma(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
Fractional atomic coordinates (x, y, z) and U_{iso} (Å ²)	
Re	(0,0,0)
U_{iso} (Re)	0.0176(7)
N1	(-0.320(3), 0.178(3), 0.1874(16))
U_{iso} (N1)	0.0163(17)
N2	(0.336(16), 0.5, 0)
U_{iso} (N2)	0.033(15)
Occupancy (N2)	0.7(2)
Calculations:	
Pressure, GPa	126
a, b, c , Å	3.488, 6.465, 6.07
V , Å ³	135.34
Re	(0,0,0)
N1	(-0.32, 0.178, 0.188)
N2	(0.34, 0.5, 0)

Figure 2. (a) Scheme of the polydiazenediyl $[-N=N-]_{\infty}$ 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; and (d) nitrogen molecules in the (001) plane in $ReN_8 \cdot N_2$ (e) Calculated electronic density of states for $ReN_8 \cdot N_2$. ($V = 135.3 \text{ \AA}^3$). (f) Calculated phonon dispersions for $ReN_8 \cdot N_2$.

Figure 3. Calculated (open symbols) and experimental (filled symbols) pressure dependence of the unit cell volume of $ReN_8 \cdot xN_2$.

The geometry of the nitrogen chains and the interatomic distances provide information about the bonding scheme in this compound. All N1 atoms have planar triangular coordination suggesting sp^2 hybridization. The N1-N1 distances are 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 $ReN_8 \cdot xN_2$ are therefore described as polydiazenediyl $[-N=N-]_{\infty}$, which can be derived from the molecular nitrogen $N \equiv N$ monomer and, to a certain extent, is a nitrogen analogue of polyacetylene^[29] and polythiazyl $(SN)_x$ ^[30] (Figure 2a).

The coordination geometry of the ReN_8 network recalls metal tetrazadiene complexes with planar MN_4 metallocycles.^[31] Such compounds are successfully stabilized at ambient conditions by substituting hydrogen atoms of tetrazadiene with organic groups, whereas neither tetrazadiene nor its organic derivatives have been isolated. In the classical approach, the ligands are 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 for a single tetraazadiene group to coordinate to a metal atom: η^4 , N-1,N-4-bridging; and N-1,N-4 metallocyclic, which is the most common geometry.^[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 ($M^{(n+2)+}/RN-N=N-NR$) and tetrazadiene ($M^{n+}/RN=N-N=NR$). The distinction between these two forms is usually made based on crystallographic information about the N-N bond lengths. Similarly, two coordination geometries exist for $ReN_8 \cdot xN_2$ (I and II in Figure 2b). The main difference between them is, in fact, the *cis*- or *trans*- configuration of the polydiazenediyl chains. For the *cis*-form (I), the $N_{\alpha}-N_{\beta}$ distances are expected to be longer than the $N_{\alpha}-N_{\alpha}$ and $N_{\beta}-N_{\beta}$ distances (see Figure 2b for the notation of N atoms). For compounds in the *trans*-form (II), the reverse is expected, i.e., the $N_{\alpha}-N_{\beta}$ distances should be shorter. In $ReN_8 \cdot xN_2$, $N_{\beta}-N_{\beta}$ and $N_{\alpha}-N_{\alpha}$ distances are slightly shorter than $N_{\alpha}-N_{\beta}$ (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 form I. The calculated charge density maps (Figure 2c) also show that there is only a very slight increase in the electron density between $N_{\alpha}-N_{\alpha}$, $N_{\beta}-N_{\beta}$ compared to $N_{\alpha}-N_{\beta}$ bonds, therefore, the bonding picture is adequately described by

scheme III (Figure 2b). In the ionic consideration, each Re atom gives four of its seven valence electrons to four N₄ units. Thus, each N₄ unit accommodates 2 electrons and has 22 valence electrons in total: four N-N σ bond pairs (8e), four dative N $\rightarrow$ 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. A delocalized π -system should give rise to metallic conductivity in ReN₈·xN₂, and this conclusion is supported by theoretical calculations (Figure 2e).

To the best of our knowledge, ReN₈·xN₂ is the first synthetic compound, that contains polydiazenediyl chains. Chains of a similar type were recently predicted in CaN₄^[33] (n^4 -coordination together with metallocyclic one), MgN₄^[18,34], 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 sp^2 and sp^3 - hybridized nitrogen atoms forming catena-poly[tetraz-1-ene-1,4-diyl] chains.^[37]

Next, we 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 $V_0 = 179.9 \text{ \AA}^3$, $K_0 = 286(16) \text{ GPa}$, $K'_0 = 2.7(2)$. We could not preserve the sample below 22.5 GPa. However, this compound can potentially be recovered at ambient pressure. This possibility is predicted by the calculated phonon dispersions (Figure 2f), which show the dynamical stability of ReN₈·N₂ for the entire pressure range (from volume $138 \text{ \AA}^3$ to $180 \text{ \AA}^3$).

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 amounts of nitrogen trapped in the channels. Indeed, the results of theoretical calculations (Figure 3b) show that the unit cell volume increases with 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, we have synthesized a novel rhenium-nitrogen compound with the highest amount of nitrogen in the Re-N system. Along with metal polyazides^[38], ReN₈·xN₂ belongs to inorganic compounds with the highest nitrogen content known to date. The synthesis of ReN₈·xN₂ is a unique example of the formation of a complex porous framework in a direct reaction between two elements, in which one of the reagents plays, in addition, the role of a guest molecule essential for the stability of the synthesized compound. These results contribute to the exploration of a 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.

Figure 4. Calculated structures of ReN₈·N₂ (a) and ReN₈ (without trapped nitrogen molecules) (b) having the same unit cell volume ($138 \text{ \AA}^3$).

Experimental Section

Synthesis

We have performed two series of experiments. In both series, a powder of Re was placed inside a $60 \text{ }\mu\text{m}$ hole in a Re gasket, preindented to a thickness of approximately $22 \text{ }\mu\text{m}$. 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 $120 \text{ }\mu\text{m}$). The first sample was compressed up to $\sim 105 \text{ GPa}$ and laser-heated up to $2300(200) \text{ K}$ (synthesis #1), whereas the second sample was compressed up to $\sim 123 \text{ GPa}$ and then laser-heated up to $2700(150) \text{ K}$ (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 ($\lambda \sim 0.29 \text{ \AA}$, Perkin Elmer XRD1621 flat panel detector).^[39] At each pressure step, we collected the X-ray diffraction images upon continuous rotation of the cell from -20° to $+20^\circ$. At selected pressure points, we collected the data with a narrow 0.5° scanning step from -38° to $+38^\circ$. We determined the pressure using the equation of state of Re.^[40] Diffraction data analysis (peak search, unit cell finding, data integration, frame scaling etc.) was performed with CrysAlis^{Pro} 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-atom ($x=0$ and 1), 42-atom ($x=3/4$) and 64-atom periodic ($x=5/6$) cells. The sampling for Brillouin zone integrations is performed using the gamma scheme with $11 \times 11 \times 11$, $6 \times 12 \times 12$ and $4 \times 12 \times 12$ 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 as 10^{-5} eV for two subsequent iterations, and the ionic relaxation loop within the conjugated gradient method was stopped when forces became of the order of $10^{-4} \text{ eV/\AA}$. The 0 K harmonic phonon calculations were performed using the finite displacement approach implemented into PHONOPY.^[48] Converged phonon dispersions were achieved using a $(3 \times 3 \times 3)$ supercell with 297 atoms and $5 \times 5 \times 5$ Monkhorst-Pack^[49] k-point sampling.

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COMMUNICATION

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