

Nitrides | Very Important Paper |

VIP Synthesis of Arsenopyrite-Type Rhodium Pernitride RhN_2 from a Single-Source Azide PrecursorMaxim Bykov,^{*,[a,b]} Kirill V. Yusenko,^[c] Elena Bykova,^[a] Anna Pakhomova,^[d] Werner Kraus,^[c] Natalia Dubrovinskaia,^[e] and Leonid Dubrovinsky^[a]

Abstract: Nitrogen-rich noble metal nitrides possess unique mechanical and catalytic properties, therefore their synthesis and characterization is of interest for fundamental solid state chemistry and materials science. In this study we have synthesized a novel single-source precursor $[\text{Rh}(\text{NH}_3)_6]_3(\text{N}_3)_5\text{Cl}_4$ (Rh/N ratio 1:11). Its controlled decomposition in a laser-heated dia-

mond anvil cell at 39 GPa resulted in a formation of rhodium pernitride RhN_2 . According to the results of single-crystal X-ray diffraction RhN_2 has arsenopyrite structure type previously unknown for this compound $[P2_1/c$ (no. 14), $a = 4.694(3)$, $b = 4.7100(6)$, $c = 4.7198(7)$ Å, $\beta = 109.83(3)^\circ$ at 39 GPa].

Introduction

Dinitrides of transition metals attract much attention due to their exceptional mechanical properties such as low compressibility and high hardness (the bulk modulus $K_0 = 428$ GPa for IrN_2 and ReN_2).^[1,2] Synthesis of such dinitrides requires very high pressure above 40–50 GPa and a simple synthetic route, which was actively exploited in the recent years, is a direct reaction between a metal and nitrogen in a laser-heated diamond anvil cell (LHDAC). This method was successfully used for the synthesis of transition metal dinitrides (PtN_2 ,^[3] PdN_2 ,^[4] IrN_2 ,^[1] OsN_2 ,^[1] TiN_2 ,^[5] RhN_2 ,^[6] RuN_2 ,^[7] CoN_2 ,^[8] CuN_2 ,^[9] FeN_2 ,^[10] CrN_2 ^[11]), polynitrides (FeN_4 ,^[10,12] ReN_8N_2 ^[13]), and alkali metal pentazoles (LiN_5 ,^[14] CsN_5 ^[15]). To scale up the production the synthesis should be carried out in a large-volume apparatus. However, a direct reaction between a metal and nitrogen cannot provide sufficient quantities of target nitrides since the amount of gaseous nitrogen that could be sealed in a capsule is too low. Therefore, use of a solid nitrogen sources turned to

be a reasonable solution. High-pressure solid-state metathesis reactions between an oxidized metal precursor and a nitride enabled the synthesis of a number of new nitride phases,^[16–20] although they have not led yet to the synthesis of highly desired polynitrides.

While single-source precursors are widely used to access nitrides of the early transition metals by chemical vapour deposition processes,^[21] examples of applying the same approach in high pressure synthesis are less common. Recently Salamat et al.^[22] demonstrated that the product of the ammonolysis of $\text{Ta}(\text{NMe}_2)_5$ [pentakis(dimethylamido)tantalum] – $[\text{Ta}(\mu\text{-NH})_a(\text{NH}_2)_b(\text{NMe}_2)_c]_n$ can be used for the synthesis of novel Ta_3N_5 polymorphs in a LHDAC.^[22] So far no single-source precursors have been reported for the synthesis of platinum-group metal dinitrides. One of the most promising single-source precursors for such synthesis could be a metal azide. Azides contain sufficient amount of nitrogen, $\text{N}/\text{M} \geq 3$, and this nitrogen is already activated, i.e. the activation barrier for the reaction is usually lower than in the reaction with triply bound N_2 molecule. Furthermore, the reaction mixture is much more homogeneous in comparison with metal/nitrogen reactions. Schnick et al. successfully used controlled decomposition of azides to obtain diazenides BaN_2 , SrN_2 and CaN_2 , as well as Li_2N_2 in a large-volume press.^[23,24] Transition metals azides and azide-coordinated transition metals salts, such as *trans*- $[\text{Pt}(\text{NH}_3)_2(\text{N}_3)_2]$ ($\text{N}/\text{Pt} = 8$)^[25] or $(\text{NH}_4)_2[\text{Pt}(\text{N}_3)_6]$ ($\text{N}/\text{Pt} = 20$)^[26] might be considered as ideal candidates for nitrogen-rich precursors. However, such compounds are difficult in preparation, extremely unstable and can be dangerous. Their loading in DACs may result in uncontrollable explosive decomposition upon compression or even before closing the cell. Alternatively, coordination compounds with N_3^- as anion are typically not explosive and can be easily prepared from appropriate chlorides by anion exchange.

In the current communication, we report the synthesis of nitrogen-rich single-source azide precursor $[\text{Rh}(\text{NH}_3)_6]_3(\text{N}_3)_5\text{Cl}_4$, with N/Rh ratio = 11. The controlled decomposition of

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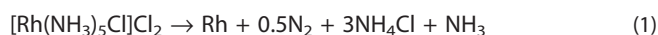
ORCID(s) from the author(s) for this article is/are available on the WWW under <https://doi.org/10.1002/ejic.201900488>.

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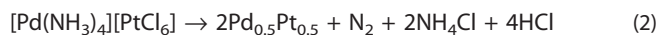
$[\text{Rh}(\text{NH}_3)_6]_3(\text{N}_3)_5\text{Cl}_4$ at high pressures in LHDAC results in a formation of rhodium pernitride RhN_2 which crystal structure was characterized by means of synchrotron single-crystal X-ray diffraction. Contrary to previous studies based on powder diffraction data and suggesting marcasite-type structure for RhN_2 , we demonstrate that RhN_2 has an arsenopyrite structure type.

Results and Discussion

Coordinated ammonia is an effective agent to reduce noble metals in coordination compounds. In solid state, ammonia-containing coordination species decompose at relatively low temperatures (below 500–600 °C) without any additional reducing agents such as gaseous hydrogen. For example, in an argon or nitrogen flow at ambient pressure, $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ decomposes with formation of Rh powder [Equation (1)].^[28]



Polymetallic coordination compounds also decompose at low temperatures in inert atmosphere that leads to formation of nanostructured multicomponent refractory alloys.^[29–31] Such compounds can be considered as perspective single-source precursors for the synthesis of multicomponent alloys, like in case of $[\text{Pd}(\text{NH}_3)_4][\text{PtCl}_6]$ [Equation (2)].^[29]



Thermal decomposition of a large selection of nitrogen-containing coordination compounds has been investigated at ambient pressure. However, to the best of our knowledge there is only one example of the formation of noble metal nitrides without addition of an extra amount of nitrogen (in form of molecular nitrogen or ammonia). So, $(\text{NH}_4)_2\text{ReF}_6$ decomposes in the argon flow above 300 °C with formation of ReNF . Above 900 °C the ReNF partially degrades further with formation of Re_3N .^[32]

In this study we have tested whether ammine complexes of noble metals, in which anions are substituted by azides, may serve as single-source precursors to polynitrides. First, we have synthesized hexaamminerhodium(III) chloride $[\text{Rh}(\text{NH}_3)_6]\text{Cl}_3$ following the procedure described in the literature.^[33] Further crystallization of $[\text{Rh}(\text{NH}_3)_6]\text{Cl}_3$ with an excess of NaN_3 did not give the expected Cl-free $[\text{Rh}(\text{NH}_3)_6](\text{N}_3)_3$ salt; instead a new compound with a composition $[\text{Rh}(\text{NH}_3)_6]_3\text{Cl}_4(\text{N}_3)_5$ was obtained. Its crystal structure (Figure 1a) can be described as a *fcc*-like ABC packing arrangement of $[\text{Rh}(\text{NH}_3)_6]^{3+}$ octahedra along the $[-110]$ crystallographic direction. All octahedral sites are occupied by linear N_3^- anions. Cl^- anions and N_3^- anions occupy 2/3 and 1/3 of the tetrahedral sites respectively. The crystal structure is similar to that of the parent compound $[\text{Rh}(\text{NH}_3)_6]\text{Cl}_3$, in which all interstitial sites of the hexagonal close packing of $[\text{Rh}(\text{NH}_3)_6]^{3+}$ ions are occupied by Cl^- anions.^[33]

Heating of $[\text{Rh}(\text{NH}_3)_6]_3\text{Cl}_4(\text{N}_3)_5$ at pressure about 39 GPa and 1600 K in a diamond anvil cell resulted in formation of multiple grains of a new phase as evidenced by a rich spotty diffraction pattern (Figure 2a). Some of these grains give diffraction pattern suitable for single-crystal XRD analysis. The methodology

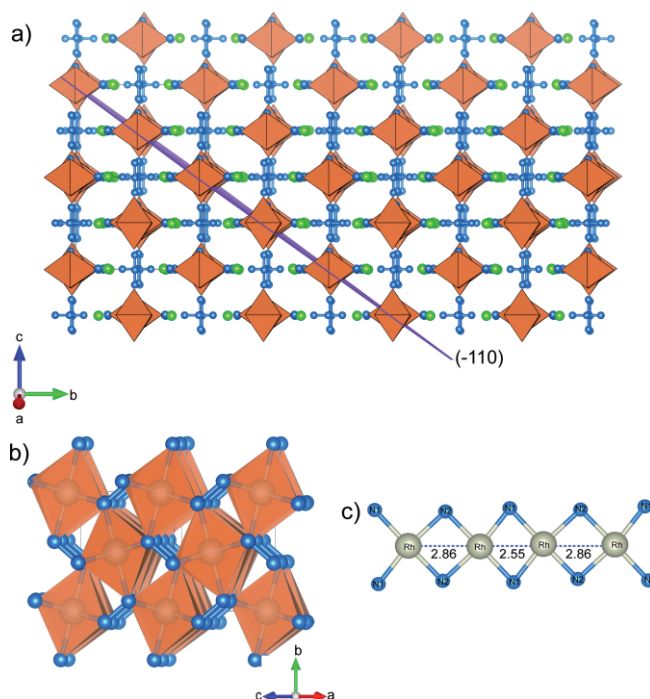


Figure 1. (a) The crystal structures of the precursor $[\text{Rh}(\text{NH}_3)_6]_3\text{Cl}_4(\text{N}_3)_5$ at ambient pressure with $[-110]$ plane shown in purple. Hydrogen atoms are not shown. Cl and N atoms are shown in green and blue respectively. $\text{Rh}(\text{NH}_3)_6$ octahedra are shown in orange. (b) The crystal structure of RhN_2 at 39.3 GPa. (c) Fragment of the crystal structure of RhN_2 at 39 GPa showing the dimerization along *a* + *c*. Short Rh...Rh distance in RhN_2 is comparable to the shortest Rh...Rh distance in a Rh metal at 39 GPa (2.55 Å in RhN_2 vs. 2.59 Å in Rh).^[27]

of the analysis of such patterns is described in detail in a number of our earlier publications.^[2,10,13,34] We were able to find the orientation matrices of several grains of the new phase. The first indexing resulted in the orthorhombic lattice parameters ($a = 3.8540$, $b = 4.7106$, $c = 2.7068$ Å) characteristic for marcasite type structure of rhodium pernitride RhN_2 .^[6,35] However, the detailed analysis of the diffraction pattern revealed several extra features that had to be explained. In particular, we observed that some of the reflections are split (Figure 2 b–d). It is a clear indication that the symmetry of the crystal cannot be accounted by orthorhombic lattice. Indeed, we found a number of reflections that do not match the unit cell of marcasite-type structure (Figure 2e–h). Instead, successful indexing was achieved with the monoclinic unit cell of the arsenopyrite-type structure [$a = 4.694(3)$, $b = 4.7100(6)$, $c = 4.7198(7)$ Å, $\beta = 109.83(3)^\circ$]. Structure solution and refinement resulted in good agreement factors ($R_1 = 0.0556$, $wR_2 = 0.0645$) for the arsenopyrite-type structure model (Table 1). To rule out the influence of Cl or H present in the single-source precursor on the crystal structure of RhN_2 , we have performed the synthesis of RhN_2 from elements at 51.7 GPa. The powder diffraction pattern (Figure 2i) clearly demonstrates that RhN_2 crystallizes in the arsenopyrite-type structure independently of the synthetic method.

The arsenopyrite structure can be obtained from the marcasite structure through a cell-doubling distortion, at which the cations in the chains parallel to *c*-axis have alternative short and long separations (Figure 1c). The basis vectors of the marcasite

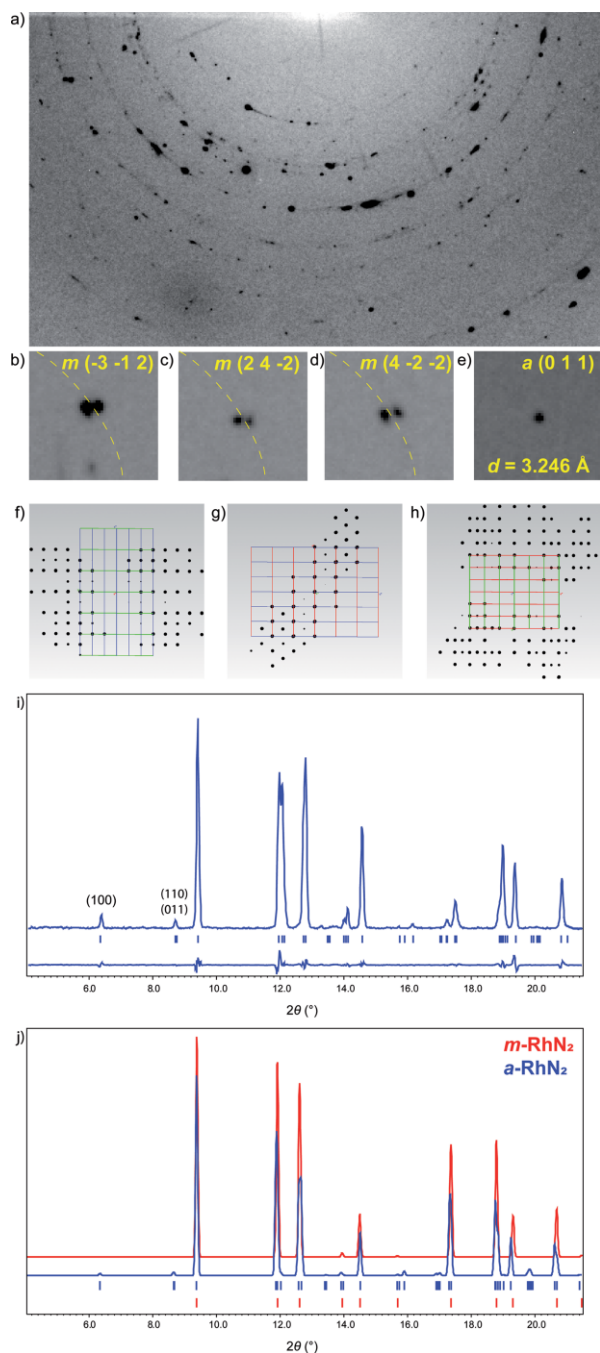


Figure 2. (a) A fragment of a typical X-ray diffraction still image of the sample after laser-heating. Most of single-crystal diffraction peaks are well separated from each other. (b–d) Certain diffraction reflections of RhN_2 are split in the radial direction at 39.3 GPa. They are well indexed for the arsenopyrite-type lattice, but would have been single peaks for the marcasite-type lattice with the indices denoted by m . Yellow dashed lines indicate circumferential directions. (e) The single “arsenopyrite” (011) reflection observed in the diffraction pattern, which would have to be absent for the marcasite-type structure. “ a ” stands for arsenopyrite type lattice (f–h) Reciprocal space views of the diffraction pattern projected along \mathbf{a}^* , \mathbf{b}^* and \mathbf{c}^* axes and superimposed by the orthorhombic lattice with the parameters $a = 3.8540$, $b = 4.7106$, $c = 2.7068$ Å, corresponding to the marcasite-type structure. As seen, this lattice does not describe all of the diffraction peaks. (i) Experimental powder diffraction pattern of RhN_2 synthesized from elements at 51.7 GPa [$\lambda = 0.4853$ Å, lattice parameters $a = 4.6664(5)$, $b = 4.6751(3)$, $c = 4.6570(4)$, $\beta = 110.88(1)^\circ$]. (j) Simulated powder diffraction patterns for marcasite-type ($m\text{-RhN}_2$, red line) and arsenopyrite-type ($a\text{-RhN}_2$, blue line) structures ($\lambda = 0.4853$ Å).

Table 1. Selected crystal structure details of RhN_2 at 39.3 GPa. Full crystallographic information is given in the supplementary cif file.

Idealized Chemical formula	RhN_2
Pressure, GPa	39.3
Space group	$P2_1/c$
a, b, c , Å	4.694(3), 4.7100(6), 4.7198(7)
β , °	109.83(3)
V , Å ³	98.16(6)
Z	4
No. of measured / independent reflections	485/199
R_{int}	0.0725
Final R indexes [$I \geq 3\sigma(I)$]	$R_1 = 0.0556$, $wR_2 = 0.0645$
Final R indexes [all data]	$R_1 = 0.0820$, $wR_2 = 0.0682$
No. of parameters	19
Rh	[0.2396(8), 0.0001(4), 0.2307(4)]
N1	[0.185(10), -0.406(3), 0.299(4)]
N2	[0.304(10), -0.588(3), 0.165(4)]

structure \mathbf{a}_m , \mathbf{b}_m , \mathbf{c}_m correspond to $\mathbf{a}_a/2$, $\mathbf{c}_a/2$, \mathbf{b}_a , $\mathbf{a}_a/2 + \mathbf{c}_a/2$ of the arsenopyrite structure, respectively.^[36] The angle between the $[10\bar{1}]$ and $[101]$ directions of the arsenopyrite-type RhN_2 may be used as a measure of the structure distortion. The deviation of this angle from the corresponding angle in the marcasite structure (90°) decreases with the pressure increase from $0.34(4)^\circ$ at 39.3 GPa to $0.12(4)^\circ$ at 51.7 GPa that is in agreement with the theoretical studies of Yu et al.^[36] Arsenopyrite structure type is typical for dipnictides of group 9 metals MX_2 ($M = \text{Co}, \text{Rh}, \text{Ir}$; $X = \text{P}, \text{As}, \text{Sb}$).^[37] Our result disagree with works of Niwa et al.,^[6,35] who reported a marcasite-type structure for RhN_2 on the basis of high-pressure powder X-ray diffraction. We should note, that it is rather challenging to recognize the peak splitting in a high-pressure powder diffraction pattern (Figure 2j), as the high-angle peaks are too weak to be clearly resolved. Moreover, a few additional weak peaks characteristic for arsenopyrite-type structure in the low- 2θ region could overlap with the peaks of $\varepsilon\text{-N}_2$ (pressure medium and reagent in Ref.^[6]). Our single crystal and powder X-ray diffraction data unambiguously prove the existence of RhN_2 with the arsenopyrite type structure, but we cannot exclude a possibility that other RhN_2 polymorphs exist at approximately the same PT conditions. The theoretical studies of Hernández et al.,^[38] for example, suggest that the calculated energy difference between the RhN_2 phases with the relaxed marcasite and arsenopyrite structures at atmospheric pressure is very small (only +0.038 eV per formula unit).

Conclusions

The advantage of the single-source precursor approach is that the precursors may be available in large quantities and can be used in large-volume press syntheses. Furthermore, the reaction with activated *in statu nascendi* generated nitrogen might lead to lowering of the pressure required for the synthesis of metastable polynitrides.^[39] A single-source precursor has a definite N/M ratio. Compared to the synthesis in a LHDAC where a metal piece is surrounded by a nitrogen fluid, the decomposition of a single-source precursor has many advantages, because inho-

mogeneity of the system in a LHDAC more likely leads to formation of a mixture of nitride phases.

On the example of RhN_2 we have shown that platinum-group metal pernitrides can be synthesized from a single-source azide precursors. High-quality single-crystal X-ray diffraction data enabled to determine the crystal structure of RhN_2 , which belongs to arsenopyrite structure type similarly to many other dipnictides of group 9 metals. The developed technique may give access to the relatively simple and reproducible synthesis of nitrogen-rich compounds of refractory metals, such as Ir, Pt, and Os.

Experimental Section

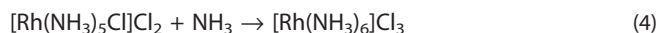
Synthesis of the Precursor

Chloropentamminerhodium(III) Chloride: $\{\text{Claus Salt}, [\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2\}$ has been prepared according to our previously published protocol [Equation (3)]:^[28]



Briefly, 1 g of $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ powder (38–41 wt.-% Rh, ABCR GmbH & Co. KG, Karlsruhe, Germany) was dissolved in 10 mL of concentrated HCl and heated for 30 minutes. After complete dissolution, 10–20 mg of solid $\text{N}_2\text{H}_6\text{Cl}_2$ (catalytic amount) was added together with 20 mL of hot ammonia buffer with pH = 8.2. Immediately, solution turned to slight yellow colour with a formation of a precipitate of $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ {precipitate might also contain minor quantities of Rh, $[\text{Rh}(\text{NH}_3)_3\text{Cl}_3]$ and $[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ }. The precipitate was filtered through a glass filter and washed from $[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ with hot water solution of HCl (2:1). Further, $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ was dissolved in hot water {insoluble Rh and $[\text{Rh}(\text{NH}_3)_3\text{Cl}_3]$ are left on the filter} and recrystallized by addition of an equal volume of 10 wt.-% water solution of HCl. After 2–3 hours, light yellow crystals of $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ were filtered and washed with ethanol, pentane and dried in air. Typical yield was 70–75 %. Phase identity was proved using powder X-ray diffraction.

Hexaaminerhodium(III) Chloride: $[\text{Rh}(\text{NH}_3)_6]\text{Cl}_3$ has been prepared according to modified procedure published in [Equation (4)]:^[33]



4 mL of 25 wt.-% water NH_3 solution was added to 0.2 g (0.7 mmol) of $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ powder in a 10 mL Teflon vial. Reaction mixture was closed in a steel autoclave (Parr Instr. Co., Molin, Ill, USA) and heated at 150 °C during 100 h. After natural cooling, reaction mixture was washed with water and evaporated on air during several days. Dry colourless powder contains pure $[\text{Rh}(\text{NH}_3)_6]\text{Cl}_3$ (according to powder X-ray diffraction). The procedure is quite general, any other rhodium(III) amines as well as rhodium(III) chloride can be used to prepare $[\text{Rh}(\text{NH}_3)_6]\text{Cl}_3$ with quantitative yield.

Hexaaminerhodium(III) Azide Chloride: $[\text{Rh}(\text{NH}_3)_6]_3\text{Cl}_4(\text{N}_3)_5$ was crystallized from water solution. 5 mg of $[\text{Rh}(\text{NH}_3)_6]\text{Cl}_3$ and 5–10 mg of NaN_3 (Sigma Aldrich) powders were dissolved in 1 mL of distilled water and evaporated during 2 weeks. Colourless 0.1 mm crystals were collected from solution. Salt is stable under mechanical impact.

The X-ray diffraction study of single crystals was performed on an automated Bruker APEX 2 CCD diffractometer (Mo-K_α radiation,

graphite monochromator, two-dimensional CCD detector) at 150 K. The structure was refined in the anisotropic approximation. Hydrogen atoms were set geometrically. All calculations were performed using SHELXTL software.^[40] In the final full-matrix refinement of 109 structural parameters total number of reflexes was used 2246 the divergence factors were: $R_{\text{all}} = 8.14\%$, $wR_{\text{ref}} = 19.52\%$; for 2097 reflections with $I \geq 2\sigma(I)$ $R_{\text{gt}} = 7.71\%$, $wR_{\text{gt}} = 19.20\%$, S factor against F^2 was 1.073. X-ray crystallographic data have been deposited with ICSD under No. 1905388.

High-Pressure Synthesis and Diffraction: A single crystal of hexaaminerhodium(III) azide chloride $[\text{Rh}(\text{NH}_3)_6]_3\text{Cl}_4(\text{N}_3)_5$ was placed inside sample chamber in a diamond anvil cell (Re gasket, initial thickness 40 μm , diameter 150 μm) along with a ruby chip that served as an internal pressure standard (Figure 3).^[41] A piece of gold was placed at the edge of the crystal and served for initial coupling of the laser radiation. Neon was used as a pressure-transmitting medium. The sample was compressed to a pressure of 39 GPa and laser-heated up to 1600(200) K with the double-sided laser-heating system of the Extreme Conditions Beamline P02.2 at Petra III (Hamburg, Germany).^[42]

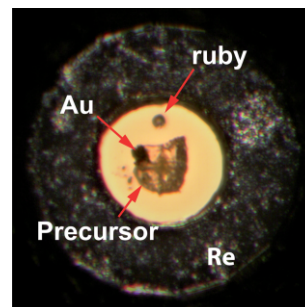


Figure 3. A microscope image of the sample chamber at ambient pressure. Hole diameter is 150 μm .

For the synthesis of RhN_2 from elements, Rh powder was loaded in a diamond anvil cell, while nitrogen served as a reagent and as a pressure-transmitting medium. The laser-heating was performed at 1500(200) K and 51.7 GPa.

Single-crystal X-ray diffraction dataset was collected at the P02.2 beamline ($\lambda = 0.29$ Å, beam size $\approx 2 \times 2$ μm^2) upon a rotation of the diamond anvil cell around the vertical ω axis with an angular step $\Delta\omega = 0.5^\circ$ and an exposure time of 1 s. Diffracted intensities were collected by a PerkinElmer XRD1621 detector. To calibrate an instrumental model i.e., the sample-to-detector distance, detector's origin, offsets of goniometer angles, and rotation of both X-ray beam and the detector around the instrument axis, we used a single crystal of orthoenstatite $[(\text{Mg}_{1.93}\text{Fe}_{0.06})(\text{Si}_{1.93}, \text{Al}_{0.06})\text{O}_6]$, P_{bca} space group, $a = 8.8117(2)$, $b = 5.18320(10)$, and $c = 18.2391(3)$ Å].

For analysis of the single-crystal diffraction data (indexing, data integration, frame scaling and absorption correction) we used the *CrysAlis^{Pro}* software package (version 171.39.46). The structure was solved with the ShelXT structure solution program^[43] using intrinsic phasing and refined with the Jana 2006 program.^[44] CSD-1908892 contains the supplementary crystallographic data for this paper.

Further details of the crystal structure investigation(s) may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fz-karlsruhe.de), on quoting the deposition numbers CSD1905388 and 1908892

Acknowledgments

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Keywords: Nitrides · Pernitrides · Polynitrides · High-pressure

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