In situ study of the high-pressure high-temperature stability field of TaN and of the compressibilities of ϑ -TaN and TaONA. Friedrich^{a*}, W. Morgenroth^a, L. Bayarjargal^a, E.A. Juarez-Arellano^b and B. Winkler^a^a*Institut für Geowissenschaften, Abt. Kristallographie, Goethe-Universität Frankfurt, D-60438 Frankfurt am Main, Germany;* ^b*Instituto de Química Aplicada, Universidad del Papaloapan, 68301 Tuxtpec, Oaxaca, Mexico*

()

The high-pressure high-temperature stability of tantalum mononitrides was investigated at 8–23.5 GPa and 1400–3500 K by in situ powder synchrotron X-ray diffraction using the laser-heated diamond anvil cell and ε -TaN as starting material. The transformation from ε -TaN to ϑ -TaN was observed and ϑ -TaN was confirmed as the stable high- (p, T) tantalum mononitride. At temperatures above 3000 K at 16–23.5 GPa the formation of a novel quenchable high-pressure high-temperature phase was observed. Under nitrogen excess ε -TaN reacted with nitrogen to the high- (p, T) phase η -Ta₂N₃ as the main stable phase at 8–13 GPa and about 2000 K. This behaviour is similar to the reaction of pure Ta with nitrogen at high- (p, T) conditions. In addition we have determined the bulk moduli of ϑ -TaN ($B = 360(15)$ GPa), which is less compressible than ε -TaN and η -Ta₂N₃, and of TaON ($B = 267(8)$ GPa).

Keywords: high pressure; tantalum nitride; tantalum oxynitride; X-ray diffraction; laser-heated diamond anvil cell; phase stability

1. Introduction

The tantalum-nitrogen system contains numerous tantalum nitride phases [1]. They have been extensively explored at high temperatures in the last decades, while fewer studies were reported on the phase stabilities at combined high pressures and temperatures. As there have been inconsistencies regarding the nomenclature of tantalum nitrides in earlier work, we refer to the nomenclature given in Friedrich et al. [1] in this manuscript.

The ground state structure of TaN is of the CoSn-structure (B35) type. This polymorph, ε -TaN, is hexagonal (space group $P\bar{6}2m$) with $a = 5.196(4)$ Å and $c = 2.911(2)$ Å [2]. The cubic high-temperature phase δ -TaN ($Fm\bar{3}m$, B1-type structure, $a = 4.32$ Å) can be formed from ε -TaN at 2273 K and 0.001 GPa nitrogen pressure, while at ambient pressure and high temperature ε -TaN decomposes to Ta₂N [3]. Other synthesis routes for the production of δ -TaN have also been explored (for a brief review see [4]), including 'rapid solid state metathesis', which gives a mixture of δ -TaN and a hexagonal phase [5], or ion irradiation [6]. In all these studies the starting compound was ε -TaN.

Two high-pressure polymorphs of TaN have been reported. Boiko and Popova [7] reported the synthesis of δ -TaN in the range of 3–10 GPa at ≈ 2073 K when hexagonal ε -TaN was used as a starting material. At lower temperatures (T in the range of 673–2073 K) they obtained ϑ -TaN in the WC-structure type ($P\bar{6}m2$).

*Corresponding author. Email: friedrich@kristall.uni-frankfurt.de

However, no further experimental details are given. Heating cubic δ -TaN in vacuum leads to a transformation to ϑ -TaN [7]. This is consistent with experiments by Brauer [8], who found the WC-structure type ϑ -TaN at high-pressure syntheses using a cylinder or belt apparatus in the pressure range of 2–10 GPa at 1073–1233 K and using ε -TaN as starting material. A further high-pressure phase of tantalum nitride, orthorhombic η -Ta₂N₃, was synthesized using Ta₃N₅ as starting material and a multi-anvil apparatus in order to generate pressures between 11–20 GPa and temperatures between 1773–1973 K [9]. In all these experiments, the analyses of the products were done *ex situ* on quenched samples.

In a recent study we have observed *in situ* the successive nitridation of tantalum by reaction of tantalum with nitrogen in a laser-heated diamond anvil cell [1]. The final reaction product at pressures up to 27 GPa and temperatures of about 2000 K was η -Ta₂N₃ as a pure and stable phase. This high- (p, T) phase is rather incompressible with a bulk modulus $B = 319(6)$ GPa [1].

With respect to the high- (p, T) stability of δ -TaN only a single temperature was reported from the quench experiments at 3–10 GPa by Boiko and Popova [7]. Hence, the aim of this study was the clarification of the relative stability of δ -TaN to ϑ -TaN at higher temperatures in the same pressure region and at both higher pressures and temperatures. The question of the relative stability of ε -TaN to ϑ -TaN and δ -TaN (B1-type structure) at high pressures was already revisited in our earlier study by parameter-free density functional theory based calculations [1]. There, we found that at ambient pressure the ε - and ϑ -phase have very similar total energies, and that the δ -phase is significantly less stable. Pressure stabilizes the ϑ -phase in relation to all other phases, and at 50 GPa the ϑ -phase is more stable than the other mononitrides by 50–100 kJ/mol. By adding temperature as an additional parameter to pressure we wanted to gain new insights into the relative stabilities of TaN phases using the laser-heated diamond anvil cell and *in situ* synchrotron X-ray diffraction. As nitrogen pressure played an important role in the high-temperature synthesis of δ -TaN [3], our experiments were performed both without and with nitrogen excess in the pressure chamber. In case of a successful high- (p, T) synthesis of δ -TaN and ϑ -TaN we intended to measure the compressibilities of both phases. However, the δ -phase was not observed in our experiments, and hence the compressibilities of ϑ -TaN and of the additionally observed TaON phase are reported in this study.

2. Experimental

An overview of the conducted experiments is given in Table 1. Small compacted powder chips of tantalum nitride were loaded into holes of 120–155 μm diameter in tungsten gaskets preindented to thicknesses of 36–49 μm in Boehler-Almax diamond anvil cells [10]. In two experiments (No. 2 and 3, Table 1) nitrogen was loaded at a pressure of 0.18 GPa within a pressure vessel as both a reaction compound and a pressure-transmitting medium. A sapphire single-crystal chip or a compressed powder layer of NaCl was placed on top of one diamond anvil for thermal insulation of the sample. Two more experiments (summarized as No. 1, Table 1) were conducted without nitrogen excess using KCl as the pressure-transmitting medium. Small pieces of ruby were loaded for pressure determination using the ruby fluorescence method [11].

Powder X-ray diffraction at high pressure and high temperature was performed at the Advanced Light Source (ALS, LBNL, Berkeley, U.S.A., beamline 12.2.2 [12]) and at PETRA III (DESY-Photon Science, Hamburg, Germany, beamline P02.2 [13]) using double-sided laser heating with two 100 W fiber lasers. At the

Table 1. Overview of the high- (p, T) experiments on compressed ϵ -TaN powder.

No.	type	synchrotron	p medium / insulation	$p_{\max}$ (GPa)	$T_{\max}$ (K)	final reaction products
1	in situ	PETRA III	KCl	23.5(1)	3500	ϑ -TaN+high- (p, T) phase
2	in situ	ALS	N ₂ / Al ₂ O ₃	13.7(1)	< 2500	η -Ta ₂ N ₃ +TaON
3	ex situ	ALS	N ₂ / NaCl	9.9(2)	$\approx$ 2000	η -Ta ₂ N ₃

ALS we used 25 keV synchrotron X-ray radiation, a $10 \times 10 \mu\text{m}^2$ beam spot and a MAR345 image plate as the detector, while at PETRA III 42.58 keV and 42.82 keV radiation, a beam focused to $2 \times 3 - 4 \mu\text{m}^2$ full width at half maximum using Kirkpatrick-Baez mirrors and a PerkinElmer XRD1621 detector were used. The laser spots had a diameter of about $30 \mu\text{m}$. In situ diffraction data were collected between ambient pressure and 23.5 GPa during and without laser heating. The final products were further analysed at ambient pressure within the diamond anvil cells and also after recovering them from the diamond anvil cells. Pressures were determined with an off-line spectrometer at ambient temperature. The determination of the temperature was problematic during the experiments at ALS, and hence only a very rough estimate of the temperature (with uncertainties of about 300 K) was obtained from visual observation. At PETRA III, however, temperatures were determined spectroradiometrically from fits to the thermal radiation with uncertainties of about 100 K. In experiment No. 3 (Table 1) one-sided laser heating was performed in Frankfurt with a 100 W fibre laser. The sample was recovered at ambient conditions, fixed with a tape within the gasket hole, and analysed at ALS. The diffraction data were processed using FIT2D [14] for integration and GSAS [15] for the refinement of lattice parameters. Intense and well-defined single-crystal diffraction spots from individual larger grains of the sample or from the diamonds as well as regions, which were shaded by the downstream laser-focusing lens during laser heating, were masked manually and excluded from the integration.

3. Results

3.1. Characterization of the starting material

Laboratory powder X-ray diffraction ($\text{CuK}\alpha_1$ radiation) of the starting material (tantalum nitride, Alfa Aesar No. 13093, purity 99.5%) at ambient conditions showed that the main portion of the material could be indexed as ϵ -TaN (>95%), while minor amounts of ϑ -TaN (1-2%), and γ -TaO (2-3%) were identified in addition. One powder pellet, which was loaded in a diamond anvil cell together with KCl and rubies for the high-pressure high-temperature measurements at PETRA III (experiment No. 1), was analysed there for spatial distribution of phases via a 7×9 point grid in $5 \mu\text{m}$ steps at 1.4(1) GPa. Again, the main phase of the sample was ϵ -TaN. The amounts of ϑ -TaN and/or γ -TaO as the minor phases varied among the measurement spots. Only three of those powder X-ray diffraction images showed few reflections which could be indexed by δ -TaN.

3.2. High- (p, T) stability of ϵ -TaN without nitrogen excess

In experiment No. 1 we profited from an extremely small X-ray beam and a good alignment of the laser optics with respect to the X-ray optics and of the visual observation path to the spectrometer slits for temperature determination. After characterization of the starting sample at 1.4(1) GPa (see above), different spots of the sample were successively laser heated by slow increase of the temperature

at pressures of about 8.2(2) GPa, 14.2(1) GPa, and 19.5(5) GPa, and on another sample at 16.1(3) GPa and 23.5(1) GPa. At each of the pressures a different sample spot, where ϵ -TaN was the main phase, was selected before laser heating was started. Only at 16.1(3) GPa the starting phase was ϑ -TaN. Generally, on temperature increase, the transformation from ϵ -TaN to ϑ -TaN was observed. Results are plotted in Figure 1. The transformation temperature measured might be overestimated in case of small deviations in the optics alignment during measurements and hence displacement of the X-ray beam from the laser beams and/or of the visual observation path from the spectrometer slits. Further, temperatures below 1500 K could not be reliably measured spectroradiometrically. Hence, the low-temperature region is ill-constrained and ϵ -TaN might be metastable there. A series of about 380 powder diffraction patterns was collected before, during, and after laser heating at the different pressures. All of them showed the disappearance of ϵ -TaN at increasing temperature and the correlated appearance of ϑ -TaN. The remaining additional reflections were indexed by KCl, the pressure medium, and varying small amounts of γ -TaO, which was already present in the starting material. No reflections indicating the presence of δ -TaN were observed on heating. At 8.2(2) GPa we observed a slow transformation from ϵ -TaN to ϑ -TaN during half an hour laser heating at around 1600 K, the lowest temperature where temperature measurement was successful, while at 2100–2450 K, pure ϑ -TaN was present immediately on laser heating. At 14.2(1) GPa, ϵ -TaN was observed up to 1560(20) K, while ϑ -TaN was stable between 2000 and 2700 K. ϑ -TaN remained present between 2000 K and 3500 K at 16.1(3) GPa. At the highest pressures of 19.5(5) GPa and 23.5(1) GPa the transformation was observed at around 1500 K and 1900–2100 K, respectively, and ϑ -TaN remained stable up to the highest temperatures of 3000–3200 K. However, at temperatures higher than 3000 K and pressures of 16–23.5 GPa additional diffraction lines appeared, which could not be indexed by the other phases or the different known tantalum nitrides, and they remained present after temperature quenching. Several heating cycles on different sample positions and at different pressures confirmed this observation, which points to the formation of a novel tantalum nitride phase at pressures of 16–23.5 GPa and temperatures above 3000 K. However, we cannot exclude the possibility of a reaction between ϑ -TaN and the pressure-transmitting medium (KCl) or carbon diffusing out from the diamond anvils as reported earlier for tantalum at about 3600 K [16]. The novel phase was present also after recovering the samples at ambient conditions (Fig. 2). Attempts to index the reflections from the new phase resulted in small unit cells of monoclinic symmetry. However, no fully satisfying solution was obtained due to the presence of additional phases (ϑ -TaN, γ -TaO, KCl) and due to a low quality of the powder diffraction images. The refined lattice parameters of ϑ -TaN at ambient conditions (Table 2) agree with the lattice parameters given by Schönberg [17] and Brauer [8] for a stoichiometry between TaN_{0.85} and TaN_{1.0}.

3.3. High-(p, T) stability of ϵ -TaN under nitrogen excess

ϵ -TaN was pressurized to about 7.6(1) GPa before laser heating started in experiment No. 2 (Table 1). The powder X-ray diffraction pattern could be indexed by an assignment of most reflections to ϵ -TaN and of few weaker reflections to tungsten, the gasket material, or δ -N₂. Refined lattice parameters are given in Table 2.

Already moderate laser heating of the sample (estimated temperature of 1500(300) K) at 7.6(1) GPa triggered the complete reaction of ϵ -TaN with the nitrogen pressure medium. η -Ta₂N₃ was identified as the tantalum nitride reaction product. Further strong reflections could be indexed with TREOR [19] and

Table 2. Selected refined cell parameters of starting and reaction products before and after laser heating. Stars (*) indicate cell parameters and errors estimated from the refinements of three powder diffraction patterns.

Compound	Space group	a (Å)	b (Å)	c (Å)	β (°)	V (Å ³)
Exp. No. 1: Starting material at 1.4(1) GPa						
ϵ -TaN	$P\bar{6}2m$	5.1889(4)		2.9014(4)		67.65(1)
γ -TaO	$Fm\bar{3}m$	4.4138(6)				85.99(4)
KCl	$Fm\bar{3}m$	6.1123(3)				228.35(3)
Exp. No. 1: Recovered sample at ambient conditions						
ϑ -TaN	$P\bar{6}m2$	2.9333(1)		2.8844(2)		21.493(2)
γ -TaO	$Fm\bar{3}m$	4.462(1)				88.81(8)
KCl	$Fm\bar{3}m$	6.296(3)				249.6(3)
novel phase	—	—	—	—	—	—
Exp. No. 2: Starting material at 7.6(1) GPa						
ϵ -TaN	$P\bar{6}2m$	5.1406(1)		2.8781(1)		65.867(3)
W	$Im\bar{3}m$	3.1272(4)				30.58(1)
δ -N ₂	$Pm\bar{3}n$	5.9319(1)				208.73(1)
Exp. No. 2: Final reaction products after decompression to 0.05(5) GPa						
η -Ta ₂ N ₃	$Pbnm$	8.1455(4)	8.2288(5)	2.9620(1)		198.54(1)
TaON	$P2_1/c$	4.9518(3)	5.0364(4)	5.1720(4)	99.517(7)	127.21(1)
W	$Im\bar{3}m$	3.153 (not refined)				31.35
Exp. No. 3: Recovered sample at ambient conditions						
η -Ta ₂ N ₃	$Pbnm$	8.151(2)*	8.18(1)*	2.9717(4)*		198.1(4)*
W	$Im\bar{3}m$	3.155(3)*				31.4(1)*

Figure 1. Schematic p - T field of TaN. The data of this study were taken from experiment No. 1 at PETRA III. Errors in temperature are about 100 K. Literature data are included from Gatterer et al. [3], Boiko and Popova [7], Brauer et al. [8] and Soignard et al. [18]. The darker shaded region and the bold dashed line represent results from quench experiments, while the lighter shaded region represents a tentative δ -TaN stability region.

were identified as the monoclinic unit cell metric of TaON (β -phase) (Fig. 2, Table 2). We assume that the oxygen, which is needed for the formation of TaON, comes from a reaction of ϵ -TaN with the insulating sapphire (Al₂O₃) layer. One or two reflections remained unindexed. They might be attributed to an aluminium-containing reaction product. Both phases, η -Ta₂N₃ and TaON, remained stable on further laser heating at higher temperatures (about 2000(300) K). Pressure and

Figure 2. Refined powder X-ray diffraction patterns (after subtraction of the background) of the reacted samples for experiment (a) No. 1 ($\lambda = 0.29118$ Å) recovered within a gasket hole, and (b) No. 2 ($\lambda = 0.4959$ Å) after decompression to ambient pressure. Arrows mark the reflections from a novel high- (p, T) phase in (a). Stars (*) mark unindexed reflections in (b). Symbols (+) represent experimental values. The result of the Rietveld fit is shown by the continuous line through the data points. Vertical bars show the positions of the allowed Bragg reflections of the different phases. The difference curve is plotted below in (b).

temperature increase to 13.7(1) GPa and >2500 K as well as decompression to ambient conditions did not lead to further phase changes. These results confirm the stability of both, η -Ta₂N₃ and TaON, at high pressures and temperatures.

In experiment No. 3 (Table 1) NaCl was used for insulation instead of Al₂O₃, and hence, no TaON could be observed in the reaction product, which contained η -Ta₂N₃. A few weak diffraction lines remained unindexed and might be attributed to the tape used to fix the sample within the gasket hole outside of the diamond anvil cell. The lattice parameters of η -Ta₂N₃ refined at ambient conditions are in good agreement with those given by Friedrich et al. [1].

3.4. Compressibilities of ϑ -TaN and TaON

Pressure-dependent unit cell parameters of ϑ -TaN were obtained from the laser heating experiments at PETRA III and during decompression (Fig. 3). Large uncertainties in pressure measurements arose from inhomogeneous pressure distribution within the pressure chamber, the use of different ruby grains, and from strain effects when using salt as pressure medium. Due to the large scatter in the data different fits of 2nd-order Birch-Murnaghan equations of state to the p - V data were

Figure 3. Pressure dependencies of the unit-cell volumes of (a) ϑ -TaN and (b) TaON. Equations of state are plotted as solid lines for fits weighted with the experimental errors of the pressures and volumes and as dashed line for a fit with equal weighting of all data in (a).

tried using the program EOSFIT [20]. A fit weighted with the experimental errors of the pressures and unit-cell volumes resulted in a bulk modulus, $B = 370(10)$ GPa, while a fit with equal weighting of all data resulted in $B = 352(13)$ GPa (Fig. 3). An averaged bulk modulus of $B = 360(15)$ GPa is suggested for ϑ -TaN from these experimental data. From our earlier quantum mechanical calculations of the elastic stiffness coefficients using density functional theory [1] a bulk modulus $B = 374(1)$ GPa was obtained for ϑ -TaN. This agrees with the experimentally determined bulk modulus within errors. The results show, that, as expected, ϑ -TaN is much less compressible than ε -TaN, the stable phase at ambient conditions ($B = 288(6)$ GPa [18]). Further, ϑ -TaN is less compressible than η -Ta₂N₃ ($B = 319(6)$ GPa [1]), which is the stable high- (p, T) tantalum nitride phase under nitrogen excess.

From our pressure-dependent unit cell data of experiment No. 2 we obtained the bulk modulus of TaON as $B = 267(8)$ GPa from a fit of a 2nd-order Birch-Murnaghan equation of state (Fig. 3). This value is in very good agreement with the theoretically computed bulk modulus $B = 280$ GPa for TaON [21].

4. Discussion of the high- (p, T) stability field of TaN

A comparison of our data measured in situ at 8–23.5 GPa and 1500–3500 K without nitrogen excess with the existing literature data of quench experiments and theoretical predictions leads to the following conclusions (Fig. 1):

Our results at 8 GPa and 1500–2400 K are consistent with those of the quench experiments by Boiko and Popova [7] and Brauer et al. [8], who observed ϑ -TaN as the stable phase at 3–10 GPa and 673–2073 K and at 2–10 GPa and 1073–1233 K, respectively. As longer heating times increased the amount of transformed sample in our experiments at a low pressure of 8 GPa and low temperature of 1600 K, a complete transformation into ϑ -TaN can be expected as a result of longer experiments. While no experimental details were given in Boiko and Popova [7], Brauer et al. [8] reported experiment times of 2–5 hours and a delayed and incomplete transformation process at low temperatures of <1073 K at 2–10 GPa, but a complete transformation at 1233 K. The formation of δ -TaN, which was observed at 3–10 GPa and 2073 K by Boiko and Popova [7], could not be reproduced in our in situ experiments up to 2400 K at 8 GPa. However, δ -TaN may be stable at lower pressures and high temperatures or at low nitrogen pressures based on earlier results [3, 7]. The use of nitrogen excess in our high- (p, T) experiments, however, did not promote the formation of δ -TaN but always led to the reaction of ε -TaN

with nitrogen and the formation of the stable nitrogen-saturated high- (p, T) phase η -Ta₂N₃. Further exploration of the TaN phase stabilities would be required at pressures < 6 GPa and temperatures > 2000 K in order to resolve the question of a possible high- (p, T) stability region of δ -TaN.

We have extended the schematic p - T field of TaN from 10 GPa and 2073 K to 23.5 GPa and 3500 K. The stable high- (p, T) phase remains ϑ -TaN up to 23.5 GPa and 3000 K. This result at high pressures and temperatures is consistent with the results of our earlier quantum mechanical calculations of the relative stabilities of TaN phases at high pressures in the athermal limit, where a stabilization of ϑ -TaN in relation to the other phases was predicted on pressure increase. The phase field at low temperatures (< 1600 K) and high pressures could not be reliably defined with our in situ experiments due to the difficulties of temperature determination at low temperatures and to the possibility of non-equilibrium conditions during laser-heating experiments. Further experiments with other methods are required in this (p, T) -field of the TaN phase diagram.

Our experiments indicate the formation of a new high- (p, T) tantalum nitride phase at pressures of 16–23.5 GPa and temperatures above 3000 K. This observation coincides with the theoretical prediction of the instability of the mononitride and formation of a novel high-pressure high-temperature tantalum nitride phase at pressures above 17–25 GPa at 2800 K from quantum mechanical computations [22]. While Kroll et al. [22] predicted a Ta₃N₅-II polymorph of the orthorhombic U₃Te₅-structure type as the stable phase, indexing of the new reflections with such a unit cell failed. Further experiments at higher pressures and temperatures are in progress in order to obtain more information on this novel phase.

Acknowledgements

Financial support from the DFG, Germany, within SPP1236 (Projects FR-2491/2-1, WI-1232/26-1), the BMBF, Germany (Projects 05KS7RF1 and 05K10RFA), and HASYLAB, DESY, Germany is gratefully acknowledged. Portions of this research were carried out at the light source PETRA III at DESY, a member of the Helmholtz Association (HGF). The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Science, of the U.S. Department of Energy under contract DE-AC02-05CH11231. This research was partially supported by COMPRES under NSF Cooperative Agreement EAR 06-49658. We thank S.M. Clark, J. Yan and V. Raju (ALS) as well as Z. Konôpková and H.-P. Liermann (PETRA III) for technical support at the beamlines and F. Schröder, N. Rademacher, J. Biehler and J.D. Bauer for their help during experiments.

References

- [1] A. Friedrich, B. Winkler, L. Bayarjargal, E.A. Juarez-Arellano, W. Morgenroth, J. Biehler, F. Schröder, J. Yan, and S.M. Clark, *In situ observation of the reaction of tantalum with nitrogen in a laser heated diamond anvil cell*, J. Alloys Compd. 502 (2010), pp. 5–12.
- [2] A.N. Christensen and B. Lebech, *A reinvestigation of the structure of ε -tantalum nitride*, Acta Crystallogr. B 34 (1978), pp. 261–263.
- [3] J. Gatterer, G. Dufek, P. Ettmayer, and H. Kieffer, *Das kubische Tantalmononitrid (B1-Typ) und seine Mischbarkeit mit den isotypen Übergangsmetallnitriden und -carbiden*, Monatsh. Chem. 106 (1975), pp. 1137–1147.
- [4] T. Mashimo, S. Tashiro, T. Toya, M. Nishida, H. Yamazaki, S. Yamaya, K. Oh-Ishi, and S. Syono, *Synthesis of the B1-type tantalum nitride by shock compression*, J. Mater. Sci. 28 (1993), pp. 3439–3443.
- [5] E. Gillan and R.B. Kaner, *Rapid solid-state synthesis of refractory nitrides*, Inorg. Chem. 33 (1994), pp. 5693–5700.

- [6] W. Ensinger, M. Kiuchi, and M. Satou, *Low-temperature formation of metastable cubic tantalum nitride by metal condensation under ion irradiation*, J. Appl. Phys. 77 (1995), pp. 6630–6635.
- [7] L.G. Boiko and S.V. Popova, *Crystal structure and superconducting properties of tantalum nitride obtained at high pressures*, JETP Lett.-USSR 12 (1970), pp. 70–71.
- [8] G. Brauer, E. Mohr, A. Neuhaus, and A. Skokan, *ϑ -TaN, eine Hochdruckform von Tantalnitrid*, Monatsh. Chem. 103 (1972), pp. 794–798.
- [9] A. Zerr, G. Miehe, J. Li, D.A. Dzivenko, V.K. Bulatov, H. Höfer, N. Bolfan-Casanova, M. Fialin, G. Brey, T. Watanabe, and M. Yoshimura, *High-pressure synthesis of tantalum nitride having orthorhombic U_2S_3 structure*, Adv. Funct. Mater. 19 (2009), pp. 2282–2288.
- [10] R. Boehler, *A new diamond cell for single-crystal X-ray diffraction*, Rev. Sci. Instrum. 77 (2006), pp. 115103/1–3.
- [11] H.K. Mao, J. Xu, and P.M. Bell, *Calibration of the ruby pressure gauge to 800 kbar under quasi-hydrostatic conditions*, J. Geophys. Res. 91 (1986), pp. 4673–4676.
- [12] W. Caldwell, M. Kunz, R. Celestre, E.E. Domning, M.J. Walter, D. Walker, J. Glossinger, A.A. MacDowell, H.A. Padmore, R. Jeanloz, and S.M. Clark, *Laser-heated diamond anvil cell at the advanced light source beamline 12.2.2*, Nucl. Instrum. Methods Phys. Res., Sect. A 582 (2007), pp. 221–225.
- [13] H.P. Liermann, W. Morgenroth, A. Ehnes, A. Berghäuser, B. Winkler, H. Franz, and E. Weckert, *The extreme conditions beamline at PETRA III, DESY: Possibilities to conduct time resolved monochromatic diffraction experiments in dynamic and laser heated DAC*, J. Phys. Conf. Ser. 215 (2010), pp. 012029/1–6.
- [14] A.P. Hammersley, S.O. Svensson, M. Hanfland, A.N. Fitch, and D. Hausermann, *Two-dimensional detector software: From real detector to idealised image or two-theta scan*, High Pressure Res. 14 (1996), pp. 235–248.
- [15] A.C. Larson and R.B. Von Dreele, *GSAS*, Los Alamos National Laboratory Report LAUR (1994), pp. 86–748.
- [16] A. Dewaele, M. Mezouar, N. Guignot, and P. Loubeyre, *High melting points of tantalum in a laser-heated diamond anvil cell*, Phys. Rev. Lett. 104 (2010), pp. 255701/1–4.
- [17] N. Schönberg, *X-ray study of the tantalum-nitrogen system*, Acta Chem. Scand. 8 (1954), pp. 199–203.
- [18] E. Soignard, O. Shebanova, and P.F. McMillan, *Compressibility measurements and phonon spectra of hexagonal transition-metal nitrides at high pressure: ϵ -TaN, δ -MoN, and Cr_2N* , Phys. Rev. B 75 (2007), pp. 014104/1–9.
- [19] N.R. Werner, L. Eriksson, and M. Westdahl, *TREOR, a semi-exhaustive trial-and-error powder indexing program for all symmetries*, J. Appl. Crystallogr. 18 (1985), pp. 367–370.
- [20] R.J. Angel, *EOS-FIT Version 5.2*, Blacksburg, USA: Virginia Tech, 2001.
- [21] J.E. Lowther, *Theoretical study of potential high-pressure phases of TaON and a quaternary $ZrTaO_3N$* , Phys. Rev. B 73 (2006), pp. 134110/1–8.
- [22] P. Kroll, T. Schröter, and M. Peters, *Prediction of Novel Phases of Tantalum (V) Nitride and Tungsten (VI) Nitride that can be synthesized under high pressure and high temperature*, Angew. Chem. Int. edit. 44 (2005), pp. 4249–4254.