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Synthesis and chemical stability of technetium nitrides

Emily Siska,[a] Dean Smith,[b] Ashkan Salamat,*[b] Keith V. Lawler,[a] Barbara Lavina,[b] Frederic Poineau,[a] and Paul M. Forster[a]

We demonstrate the synthesis and phase stability of TcN, Tc$_2$N, and a substoichiometric TcN$_x$ from 0–50 GPa and to 2500 K in a laser-heated diamond anvil cell. At least potential recoverability is demonstrated for each compound. TcN adopts a previously unpredicted structure identified via crystal structure prediction.

Compared to neighboring elements, little is known regarding the fundamental chemistry of technetium, the lightest element with no stable isotopes. This deficiency serves as an obstacle to reliably modeling Tc reactivity and behavior, thus designing nuclear waste storage forms with long-term chemical stability. The range of chemistry exhibited by Tc is unique with a remarkable number of oxidation states (nine) ranging from -1 to +7. At higher oxidation states for Tc binary compounds, the bonding is known to be intermediate between the strongly covalent bonding found for manganese and the ionic bonding known for rhenium.[1] However, there have been only a limited number of Tc binary compounds reliably reported, and nearly all on oxide and sulfide chemistries.[1]

Only one technetium nitride has been previously claimed; a nitrogen-poor compound from two reported preparations: reducing NH$_4$TcO$_4$ in hydrogen and then heating in ammonia at 900-1100 °C,[2] and thermal decomposition of (NH$_4$)$_2$TcX$_6$ (X= Cl, Br) at 380 °C under Ar.[3] The resulting black, brittle compound was indexed with an *fcc* cubic rocksalt structure. Using measured unit cell constants that range between 3.980 and 3.985 Å, a composition near TcN$_{0.76}$ was suggested. This has not been re-determined since it was claimed 50 years ago. In fact, a computational study found a mismatch with the predicted lattice and the experimental claims for TcN$_{0.76}$, leading to the assertion that only subnitrides (i.e. Tc$_3$N and Tc$_2$N) could be formed at ambient conditions.[4] This was later confirmed by an evolutionary algorithm structure search that showed only Tc subnitrides might be accessible at ambient, but elevated pressure is needed to obtain higher nitrogen content.[5]

Of the recently discovered *4d* and *5d* transition metal nitrides, many are only accessible via high pressure and temperature (HPHT) pathways.[6–8] Thermochemical reactivity of metals with nitrogen under extreme conditions permits a vast exploration of metastable stoichiometric phase-space. With pressure, the chemical potential of nitrogen increases dramatically, permitting the opportunity for tailored metal/nitrogen content and fine tuning of physical properties.[9] This approach for the formation of radionuclide metal nitride compounds is promising for waste form development, with implications in material and medical sciences.[10] The expected difficulties in accessing and handling ^{99}Tc often mean that rhenium is used as an analog owing to their similar ionic radii and preferred oxidation states.[1] Re–N exploratory chemistry has revealed the necessity for a combination of HPHT conditions for the synthesis of stoichiometric (meta)stable rhenium nitride compounds.[11,12] At moderate pressures (below 30 GPa) two rhenium nitrides were reported using elemental starting materials (Re foil in a nitrogen environment) in a diamond anvil cell (DAC) and laser heated under pressure.[11] Re$_3$N and Re$_2$N are both indexed as hexagonal, the same as the parent Re structure – typical behavior of subnitrides — with $P\bar{6}m2$ and $P6_3/mmc$ symmetry, respectively.

We report the high-temperature, high-pressure synthesis of the first two stoichiometric technetium nitride compounds TcN, Tc$_2$N, as well as a substoichiometric TcN$_x$ previously observed during the recent synthesis of a second Tc allotrope.[13] TcN$_x$ is fully recoverable and Tc$_2$N and TcN are potentially recoverable, remaining in their high density phase, at ambient conditions. Reaction products are monitored using *in situ* synchrotron x-ray diffraction measurements during laser heating, under high pressure, in the DAC. Each compound is characterized using Rietveld structural refinement across a range of conditions. The experimental work is supported by crystal structure predictions (CSP) as justification for the structural determination. Our

a. Department of Chemistry and Biochemistry, University of Nevada, Las Vegas, Las Vegas, NV 89154, USA

b. Department of Physics and Astronomy, University of Nevada, Las Vegas, Las Vegas, NV 89154, USA. E-mail: salamat@physics.unlv.edu
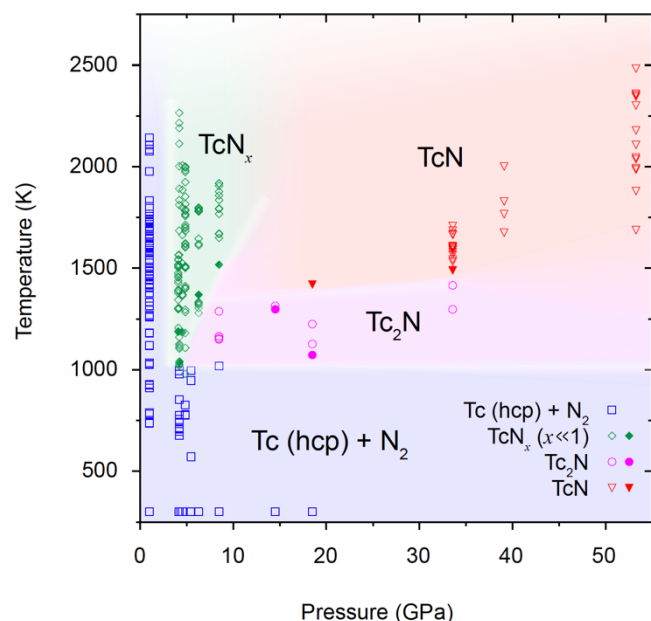
Figure 1: High P/T mapping of phase stability domains of Tc–N compounds. Solid symbols represent points of synthesis. Hollow symbols represent heating of an already transformed compound. Shaded regions represent a suspected stability domain for a particular compound. Two of the data points for TcN_x are taken from Ref. [13].

simulations identify an orthorhombic (*Pnma*) ground state solution for the mononitride, counter to the trends demonstrated by other chemically equivalent *4d* and *5d* systems. Our work identifies pathways to increase the fugacity in nitrogen to permit controlled Tc-N chemistry and the thermodynamic pathways necessary to access these compounds.

Technetium metal aggregates are heated in a nitrogen environment, under high pressure conditions, using a near-infrared laser heating system while tracking transformations using *in situ* synchrotron XRD.[14] The three distinct technetium compounds, TcN_x, Tc_2N, and TcN are formed between 4 and 50 GPa at temperatures up to 2500 K. All compounds were confirmed with multiple laser heating runs, with a total of 17 different samples prepared. Structure and stoichiometry are confirmed by Rietveld refinement, and supported by reported structure predictions.[4] Mapping the experiments on a pressure-temperature plot (Figure 1) naturally elucidates the phase stability domains.

Reaction of *hcp* Tc metal with N_2 is observed above 4.2(2) GPa and 1041(50) K forming a sub-stoichiometric nitrogen-poor metal nitride, TcN_x (x<<1) with the Tc sublattice adopting an *fcc* ($Fm\bar{3}m$) structure. The steep, positive stability boundary shows no temperature dependence over a very narrow pressure range. Transformation to TcN_x is no longer observed above 9 GPa. However, once quenched to ambient conditions, this phase persists at room temperature to upwards of 50 GPa. Rietveld refinement of TcN_x with an *fcc* ($Fm\bar{3}m$) structure at ambient yields a=3.9461(2) Å (V=61.45(4) Å^3) with a wR=1.52% and Tc atoms on the 4a Wyckoff position (Figure 2a).

The cell volume of this TcN_x phase is much higher (15.4 Å^3 per Tc) than is expected compared to the elemental *hcp* phase (14.3 Å^3 per Tc). The reason for this is not nitrogen content, but

rather that TcN_x is related to a second, recently characterized allotrope of Tc, β-Tc.[13] β-Tc, initially synthesized in Ar, has a tetragonally distorted *fcc* cell with an anomalously large volume at ambient temperatures (V_0 of 15.9 Å^3 per Tc). In this context, TcN_x can be seen as nitrogen imbued β-Tc as signified by milder synthesis conditions and an anomalously lower volume than pure β-Tc.[13] The concentration of N is so low in the samples that there is insignificant data in the XRD patterns to refine a higher symmetry than the *fcc* Tc sublattice. However, It is common in non-stoichiometric nitrides for the parent metal lattice to contain nitrogen atoms randomly distributed on interstitial sites (Figure 2b)[15] Energy-dispersive X-ray (EDX) spectroscopy employed on a TcN_x sample recovered from a LH-DAC revealed no detectable amount of nitrogen in the sample,[13] suggesting a nitrogen content somewhere between 0-2 atom %.

Synthesis of Tc_2N is observed as low as 8.5 GPa and 1000 K. As seen in Figure 1, the compound has a narrow finite thermodynamic corridor between approx. 1000 and 1400 K outside of which it transforms to either TcN_x (at lower pressures) or TcN (at higher pressures). Tc_2N persisted to upwards of 50 GPa at room temperature. The Tc_2N structure is analogous to previously observed Re_2N with a similar stability regime.[11] A full Rietveld refinement (Figure 2b) was carried out using the hexagonal ($P6_3/mmc$) structure model at 14 GPa with Tc on Wyckoff position 4f (u=0.108) and N on 2d; the refined lattice has a= 2.760(2) Å and c = 9.63(4) Å (V = 63.54(5) Å^3) with a wR = 1.33% (Figure 2b). The material can be described as an *hcp* Tc lattice with nitrogen intercalated into the host lattice that rest in tetrahedral sites (Figure 2d,e).

Transformation to TcN is only observed at pressures above 10 GPa and always from the Tc_2N phase. The material persists through compression and multiple laser heating cycles to upwards of 50 GPa. This material could be reasonably fit with the hexagonal nickel arsenide (NiAs, $P6_3/mmc$) or tungsten carbide (WC, $P\bar{6}m2$) structural models previously evaluated for TcN,[4] although neither was able to reproduce the lowest 2θ features. Experimentally, the difference between the two structure models could not be determined within the resolution of the measurements. Thus, CSP simulations were performed at 40 GPa with USPEX[16] using plane wave density functional theory (DFT) with VASP and the PBE[17] functional with a single parameter Hubbard +U (3.5 eV)[18] correction applied to the Tc *d* electrons (full details in the Supplemental). The lowest energy structure yields a third possible solution, orthorhombic *Pnma*. All three solutions have a trigonal prismatic structural motif and yield very similar diffraction patterns (plots in Supplemental). However, it is only the lower symmetry *Pnma* solution that accounts for the lowest peak below 6 degrees 2θ. Full Rietveld refinement with the orthorhombic (*Pnma*) structure model at 39 GPa gives a=5.4394(2) Å, b=2.7191(3) Å, c=4.7224(6) Å (V=69.847(3) Å^3), and Tc on Wyckoff position 4c (u=0.0168(7), w=0.2618(6)) and N on 4c (u=0.764(5), w=0.074(1)) with a wR=1.79%.

CSP predicts the *Pnma* structure to be more favorable than the more conventional, related NiAs structure by only 10.5 meV per formula unit; the previously predicted $R\bar{3}m$ structure is the third most favorable.[5] Re-evaluating the relative stabilities of
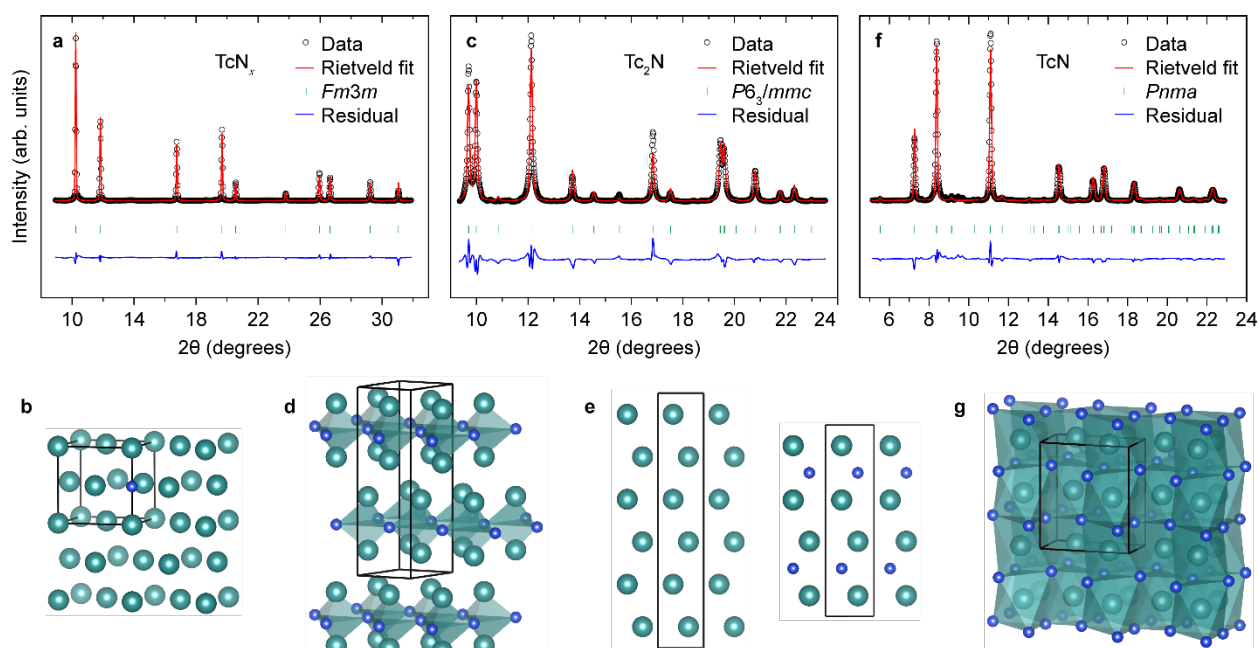
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Figure 2: Structural refinements and representation of technetium nitride compounds. Refined data points are shown as black dots and the Rietveld fit as a red line. The difference plot is shown as a blue line below the diffraction pattern with the allowed reflections shown as green tick marks. **a** Rietveld refinement of recovered TcN_x ($x<<1$) at ambient pressure with an *fcc* Tc lattice (*Fm$\overline{3}$m*). Data was collected with $\lambda = 0.4066$ Å. **b** Structural representation of TcN_x. **c** Rietveld refinement of Tc_2N at 14 GPa in nitrogen with *P6$_3$/mmc* symmetry. Data was collected with $\lambda = 0.4066$ Å. **d** Structure of Tc_2N. **e** Unit cells of hcp Tc and Tc_2N projected along a, showing the intercalation of N between Tc layers in ABA stacking. **f** Rietveld refinement of TcN at 39 GPa in nitrogen with. *Pnma* symmetry. Data was collected with $\lambda = 0.3445$ Å. **g** Structure of TcN.

the structures without the Hubbard +U correction narrows the energy differences, making the *Pnma* structure more favorable than the NiAs structure by 4.7 meV per formula unit. Despite remaining more favorable, the inclusion of the +U correction is likely the reason that the *Pnma* structure was identified by our CSP. Converting the NiAs hexagonal structure into an orthorhombic cell and shifting it to be commensurate with the *Pnma* structure shows that the atoms in the *Pnma* structure only subtly distort away from their higher symmetry positions in the NiAs structure (Figure 3). Phonon calculations identify the origin of the favorable low symmetry distortions as a dynamic instability in the NiAs structure at the M point of the Brillouin zone and possible Kohn anomalies in the Γ-K and Γ-M directions The *Pnma* structure is dynamically stable.

Figure 4 provides the pressure-volume relations for all three nitrides synthesized compared to elemental *hcp* Tc.[19] The volume per Tc atom can be directly correlated to the nitrogen content, as the unit cell increases with the addition of anions. Tc_2N and TcN were first brought to ambient conditions and then reloaded in a helium pressure transmitting medium to ensure quasi-hydrostatic conditions for compression at higher pressures (further details in Supplemental). While Tc_2N and TcN were not directly measured at ambient pressure their persistence after a DAC transfer indicates they are likely fully recoverable to ambient. All three nitride phases are fitted to a second-order Birch-Murnaghan equation of state giving bulk moduli of 298(4), 342(8) GPa, and 322(6) GPa for TcN_x, Tc_2N and TcN respectively. Note, TcN_x compression was measured previously in N_2.[13] The PBE+U bulk moduli are in good agreement at 332 and 324 GPa for Tc_2N and TcN, respectively. These nitride materials are not nearly as incompressible as their experimentally confirmed rhenium counterparts, a trend

previously seen computationally across the group 7 M_2N materials attributed to a decreasing coupling between the M–N–M layers going up the group.[20]

No transformations between elemental *hcp* Tc and nitrogen below 4.2(2) GPa were observed. Attempts at melting Tc in nitrogen below these pressures in the LH-DAC, and rapid quenching did not reveal any evidence of a reaction as confirmed by both Raman spectroscopy and XRD. Our findings neither confirm any phase as given by the previous CSP[5] and lead us to believe that the previous reports of an *fcc* technetium nitride compound are most likely a consequence of impurities and not the formation of a pure binary compound. The likely reaction in such experiments often leads to the formation of a metal oxynitride. This is consistent with previous work in which Tc with an *fcc* structure was observed at low temperatures (380–600 °C) but transformed to *hcp* at higher temperatures
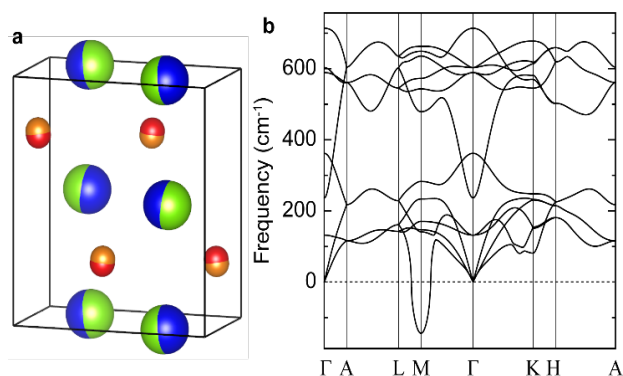

Figure 3: (left) Overlay of the TcN atomic positions in the NiAs (blue – Tc, red – N, adjusted to orthorhombic lattice scaled to match that of *Pnma*) and *Pnma* (green – Tc, orange – N) PBE+U structures. (right) PBE+U phonon band structure for TcN in the NiAs structure at 40 GPa.
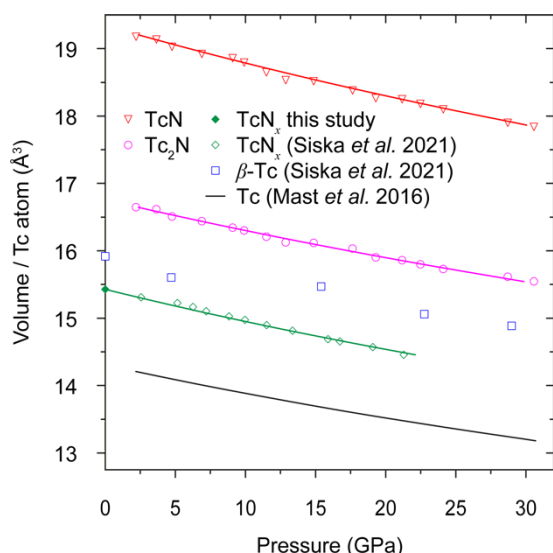
Figure 4: Volume per Tc atom as a function of pressure of the three nitride phases compared. All phases were fitted with a second-order Birch-Murnaghan equation of state.

(800 °C).[3] Other possibilities cannot be ruled out from the previous reports as their synthesis route of thermal decomposition to elemental Tc could also have residual N, H, O in the system, leading to non-binary non-stoichiometric compounds. This does however, lead to a new and exciting field of synthesizing chemically-stable Tc compounds at more moderate temperatures and pressures.

Three different binary compounds of Tc–N were synthesized up to 50 GPa and 2500 K using the laser heated diamond anvil cell and characterized *in situ* using x-ray synchrotron diffraction and supported by DFT calculations. Two of these are previously unreported stoichiometric nitrides, Tc_2N and TcN. The structure for Tc_2N is analogous Re_2N. TcN forms in a newly identified *Pnma* structure, which is a lower symmetry modification of the NiAs structure type found in other transition metal mononitride and monocarbides. This low symmetry distortion is a consequence of dynamic phonon instabilities. The third phase is a non-stoichiometric, nitrogen-poor TcN_x (x<<1) system with an *fcc* Tc lattice. That no Tc–N chemistry is observed below 4 GPa indicates previous reports of Tc nitrides are, in fact, complex multi-elemental compounds arising from the precursor starting materials.

Conflicts of interest

There are no conflicts to declare.

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