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Combining metastable precursors with high pressure-temperature treatment is a powerful tool to make nitrogen-rich metal nitrides. Two new dense polymorphs of Ta₃N₅ have previously been theoretically predicted, with U₃Se₅ (Pnma) and U₃Te₅ (Pnma) structure types, and are now shown to exist. Amorphous Ta₃N₅ from thermal ammonolysis of an amorphous polymeric precursor was laser heated at 22 GPa and examined using synchrotron X-ray diffraction to reveal the emergence of these two novel polymorphs.

The maximum observed metal oxidation state in transition metal nitrides is typically lower than that found in the oxides. Prior to 2003 Ta₃N₅ and Zr₅N₄ were the only well characterized examples of nitride compounds with the metal in its maximum oxidation state, as these phases form via elevated temperature reactions of the metal chloride (Ta and Zr) or oxide (Ta) with ammonia. Unlike metallic lower nitrides these compounds are semiconductors giving rise to optoelectronic applications. For example Ta₃N₅ is an orange-red pigment that has been extensively studied for its visible light photocatalytic activity.

The application of synthesis in diamond anvil cells (DACs) to high oxidation state transition metal nitrides was first described by Zerr et al., who used laser heating (LH) to combine elemental Zr and Hf with nitrogen at high pressure and obtain the Th₅P₄-type Zr₅N₄ and Hf₅N₄ phases. The cubic Zr₅N₄ polymorph has extremely high hardness and has since been produced by thin film techniques. Analogous methods have since been applied to obtain W₅N₃, W₅O₃, Re₅N₄ and the first platinum group metal nitrides. It is important to develop the solid state chemistry of such high oxidation state nitrides in our search for new materials with important electronic and high hardness properties.

Synthesis of U₃Se₅ and U₃Te₅ type polymorphs of Ta₃N₅ by combining high pressure–temperature pathways with a chemical precursor approach

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Combining metastable precursors with high pressure-temperature treatment is a powerful tool to make nitrogen-rich metal nitrides. Two new dense polymorphs of Ta₃N₅ have previously been theoretically predicted, with U₃Se₅ (Pnma) and U₃Te₅ (Pnma) structure types, and are now shown to exist. Amorphous Ta₃N₅ from thermal ammonolysis of an amorphous polymeric precursor was laser heated at 22 GPa and examined using synchrotron X-ray diffraction to reveal the emergence of these two novel polymorphs.

The tantalum-nitrogen system includes the subnitride Ta₃N, several TaN polymorphs, Ta₅N₆, Ta₇N₅, Ta₂N₃ and Ta₃N₅. Density-functional theory (DFT) calculations by Kroll et al have predicted that the known Cmcm Ta₅N₆-I semiconducting phase should transform into a metallic Ta₅N₆-II polymorph with the U₃Te₅ structure at ~10 GPa. A second U₃Se₅ structured phase lies at similar energy at this pressure and a further transformation into the Sm₅SnS₅ structure type could occur above 20 GPa (Fig. 1). Previous attempts to obtain these phases by high pressure-high temperature synthesis from the elements or Ta₅N₆ have only succeeded in producing Ta₃N₅. Here we report the first evidence of U₃Se₅- and U₃Te₅-structured Ta₅N₆ using LH-DAC techniques combined with a chemical precursor approach.

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approaches. In our recent synthesis of two high pressure HfN₄ polymorphs we took a nanocrystalline HfN₄ material made by pyrolysis of such a polymer in ammonia, and laser heated it under pressure to produce new crystalline phases identified by synchrotron XRD. Solution phase reactions of Ta(NMe₃)₅ with ammonia proceed via transamination and condensation to produce a polymeric solid with variable amounts of bridging imide, terminal amide and terminal dimethylamide groups.⁴¹,²²

\[ n \text{[Ta(NMe₃)₅]} + (a+b)n \text{NH}_3 \rightarrow \text{[Ta(μ-NH)₃(NH)₃(NMe₃)]ₙ} + (5-c)n \text{HNMe₂} \]

Firing the yellow precipitate in ammonia resulted in broad diffraction features at lower temperatures followed by crystallisation of the known Cmcm phase of Ta₃N₅ at 800 °C (Fig. 2). Rietveld fitting of this pattern shows the material to be identical to that produced conventionally by ammonolysis of Ta₂O₅. The UV-visible spectrum of this maroon-coloured sample (Fig. 2) shows an absorption edge at ~600 nm corresponding to an optical band gap of 2.07 eV (2.08 eV for Ta₃N₅ obtained from Ta₂O₅).⁵ The broad X-ray feature between ~25-40° 2θ (maximum near d = 2.71 Å) observed for samples made at 500-700 °C indicates amorphous material.

![Fig. 2](https://example.com/fig2.png)

**Fig. 2** PXD patterns (λ = 1.5406 Å) of the tantalum nitrides obtained by firing the polymer precursor under ammonia at various temperatures. The reflections observed after firing at 800 °C match those expected for the Cmcm phase of Ta₃N₅. Inset: The UV-visible spectrum of crystalline-Ta₃N₅ obtained by firing the polymer precursor under ammonia at 800 °C.

Combustion analysis of the crystalline Ta₃N₅ sample produced at 800 °C showed 11.5% N (theoretical 11.4% for stoichiometric Ta₃N₅) with no C or H (<0.1%) present. Samples heated at 500, 600 and 700 °C contained 0.8-0.9% C, no H and 12.3 (500 °C), 12.9 (600 °C) or 13.5% (700 °C) nitrogen. Thermogravimetric analyses showed negligible (<0.2%) mass loss, indicating that all or most amide/imide groups present in the starting polymer material had decomposed at these temperatures. All samples decreased in weight above ~750 °C due to nitrogen loss as observed for crystalline Ta₃N₅ transforming to TaN.

The 500 °C Ta₃N₅ amorphous precursor sample was chosen for high pressure-high temperature studies as similar compositions were obtained at all temperatures and local order was likely to be minimized at the lowest annealing temperature. The broad main diffraction feature moves to slightly higher d-spacing on initial compression, before steadily decreasing above ~5 GPa. This is consistent with an initial coordination increase in the densified amorphous material followed by general shortening of the Ta-N bond lengths with pressure. The sample was then heated at 20 GPa at ~1500-2000 K for several minutes using a CO₂ laser before the XRD pattern was collected ex situ at ambient temperature. A series of sharp crystalline peaks had replaced the broad amorphous pattern (Fig. 3). Initial crystallographic examination strongly indicated the presence of the predicted U₅Se₅ phase and a series of Rietveld refinements was carried out to test the likely presence of other candidate structures, using literature lattice parameters where these were known in this pressure range (key fits shown in supplementary information).

![Fig. 3](https://example.com/fig3.png)

**Fig. 3** XRD patterns (λ = 0.411 Å) of (a) amorphous Ta₅N₅ at 20 GPa (the broad feature is centred on d = 2.56 Å at this pressure) and (b) crystalline tantalum nitride after laser heating at 1500-2000 K and 22 GPa. The Rietveld fit to the data (upper black line) after laser heating is shown in red, and the difference plot as the lower black line (Rwp = 23.39% and Rsf = 19.80%). The red tick marks and XRD trace (c) show the allowed reflection positions and refined profile of the U₅Se₅ phase of Ta₅N₅ (Pnaa, a = 8.802(3), b = 6.044(4) and c = 5.492(3) Å). The green tick marks and XRD trace (d) show the same information for the U₅Te₅-type phase (Pnaa, a = 9.944(2), b = 2.691(6) and c = 9.015(6) Å).

Neither the known ambient pressure (Cmcm) Ta₃N₅-1 phase nor the Sm₅Sn₅ phase which Kroll predicted to be the third most stable (Fig. 1) yielded a good fit to the data. The major peaks were also not consistent with the decomposition of the sample to the lower nitride compositions of TaN or Ta₃N₅. The best fit to a single phase was obtained using the U₅Se₅-structured phase, and the U₅Te₅ form was the only secondary phase that could fit the shoulder on the right-hand side of the most intense peak at 9.3°. Hence our structural characterisation at ambient temperature following high P,T transformation confirms the presence of the two lowest energy phases predicted by Kroll to exist between 10-20 GPa.¹⁸ The U₅Se₅- and U₅Te₅-type structures are present in approximately equal amounts and the unit cell parameters correspond closely with DFT predictions.¹⁸ Both the predicted U₅Se₅ and U₅Te₅ phases are calculated to become stabilized above ~10 GPa and remain close in energy throughout the 10-20 GPa range (Fig. 1) so that the simultaneous presence of both polymorphs following high pressure-high temperature synthesis is to be expected. Atom positions were taken from the known U₅Se₅ and U₅Te₅ structures²⁶,²⁷ and were not refined further due to the limited 20 range and overlapping patterns.
Previous attempts to synthesize the high-density \( \text{Ta}_3\text{N}_5 \) polymorphs applied \( \text{LH-DAC} \) to elemental \( \text{Ta} + \text{N}_2 \) at 2000 K and up to 27 GPa\(^{20}\) or multianvil high-P, T treatment of \( \text{Ta}_3\text{N}_5 \) at 1800-2000 K and 9-11 GPa.\(^{19}\) Both approaches resulted in formation of the lower nitride phase \( \eta \)-\( \text{Ta}_2\text{N}_3 \). The P, T conditions of most of these experiments lie within the stability range of \( \text{Ta}_2\text{N}_3 \) predicted by Kroll,\(^{1,28}\) although Friedrich’s\(^{50}\) highest pressure experiments lie close to the \( \eta \)-\( \text{Ta}_2\text{N}_3 \) stability boundary according to Kroll’s calculations. Close examination of our data reveals that a small amount of \( \eta \)-\( \text{Ta}_2\text{N}_3 \) is in fact present along with a small amount of \( \varepsilon \)-\( \text{N}_2 \), produced by thermal decomposition of the \( \text{Ta}_3\text{N}_5 \) starting material along with the high P, T crystallisation into \( \text{U}_4\text{Se}_5 \)- and \( \text{U}_4\text{Te}_5 \)-structured phases (Fig. 4). Le Bail fitting of these additional phases reveals lattice parameters of \( a = 8.082(5) \), \( b = 8.051(5) \) and \( c = 2.934(8) \AA \) for \( \eta \)-\( \text{Ta}_2\text{N}_3 \), and \( a = 7.323(6) \) and \( c = 9.894(5) \AA \) for \( \varepsilon \)-\( \text{N}_2 \), both consistent with expectations for these phases at the pressures used.\(^{32,33}\)

Our synthesis experiments were conducted inside the closed \( \text{LH-DAC} \) environment using a chemically-produced amorphous precursor with the target stoichiometry and this appears to have been important in achieving the first synthesis of these theoretically predicted phases. Considering the calculated \( \text{Ta}_3\text{N}_5 \)-II stability field\(^{28}\) and the low level of decomposition to \( \eta \)-\( \text{Ta}_2\text{N}_3 \), it is likely that the temperature experienced by the main part of the sample during our laser heating process was at the lower end of the 1500-2000 K range that we have estimated for the experiment. It is not yet possible to determine the relative stability relations between the \( \text{U}_4\text{Se}_5 \)- and \( \text{U}_4\text{Te}_5 \)-structured forms because of their closely overlapping enthalpy-pressure relations. In our experiments both were obtained simultaneously. However delicate tuning of the amorphous precursor along with precise control over the P, T synthesis conditions might selectively produce the \( \text{U}_4\text{Se}_5 \) and \( \text{U}_4\text{Te}_5 \) phases. The first order nature of the phase transitions indicates that these structures could be recoverable to ambient conditions although that could not be investigated here due to experimental constraints.

The high pressure-high temperature crystallisation of an amorphous/nanocrystalline \( \text{Ta}_3\text{N}_5 \) precursor results in the first synthesis of two new high-density crystalline polymorphs. These were predicted to exist theoretically but had not been achieved previously using approaches including high-P, T synthesis from the elements or low pressure phases. Our approach represents a versatile technique that can be obtained to obtain other highly nitrided compounds with the metals in high oxidation states and high coordination numbers. The previous theoretical investigation indicated that the high pressure \( \text{Ta}_3\text{N}_5 \)-II phases should have metallic properties.\(^{18}\) This is in agreement with the high optical reflectivity and lack of obvious Raman features observed experimentally (see Supplementary Information). That would make it unsuitable for photocatalysis applications but the conducting powders could have catalytic properties, as found for other transition metal nitrdes including MoN.\(^{29}\) Furthermore, the theoretically calculated bulk modulus of the \( \text{Ta}_3\text{N}_5 \) with the \( \text{U}_4\text{Te}_5 \) structure type of 378 GPa describes a highly incompressible material with potentially useful mechanical applications.\(^{18}\)

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### Notes and references

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\(^{\dagger}\) Brief experimental details: A polymeric precursor to \( \text{Ta}_3\text{N}_5 \) was obtained from \( \text{Ta}(\text{MnC}_2) \) and ammonia similarly to a previous report.\(^{22}\) The sample was then fired under dry flowing ammonia at 500, 600, 700 or 800 °C for 2h. Powder X-ray diffraction (PXD) patterns were collected under \( \text{N}_2 \) with a Siemens D5000 using Cu-K\( \alpha_1 \) radiation (\( \lambda = 1.5406 \) Å) and a sample holder for air sensitive material and data were refined using GSAS.\(^{30}\) Combustion analysis of the amorphous \( \text{Ta}_3\text{N}_5 \) precursor was by Medac Ltd. Diffuse reflectance UV-visible spectra were obtained using a Perkin Elmer Lambda 35 spectrometer with an integrating sphere. Raman spectra were recorded using an InVia Renishaw spectrometer with an excitation wavelength 785nm (diode laser) (see ESI). High pressure experiments were carried out in a symmetrical Mao-type cell using brilliant cut type Ia diamonds with 300 µm culets. For pressure measurements, the ruby fluorescence peak was excited by Ar\(^2\) laser radiation of wavelength 514.5 nm. The amorphous precursor was treated under \( \text{N}_2 \) with a Siemens D5000 using Cu-K\( \alpha_1 \) radiation (\( \lambda = 1.5406 \) Å) and a sample holder for air sensitive material and data were refined using GSAS.\(^{30}\)

Electronic Supplementary Information (ESI) available: Full sample preparation details, infrared spectrum and TGA of the polymer precursor,
TGA traces and TEM images of tantalum nitride samples fired at various
values, Rietveld fit to the 800 °C sample, Raman spectra before and
after laser heating. XRD of the amorphous sample during
compression and full crystallographic results for the mixture of new
TaNi polymorphs. See DOI: 10.1039/c000000x
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