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Supporting information: Synthesis of U₃Se₅ and U₃Te₅ type polymorphs of Ta₃N₅ by combining high pressure-temperature pathways with a chemical precursor

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A polymeric precursor to Ta_3N_5 was obtained by reacting a solution of $Ta(NMe_2)_5$ (2 g, Epichem) in dry THF (20 cm³) with liquid ammonia (20 cm³, distilled from sodium) under nitrogen at -78 °C with continuous stirring, similarly to a previous report.¹ The reaction mixture was left to come to room temperature as the excess ammonia evaporated, and the yellow tantalum imide/amide polymer (~1.2 g) was filtered and dried under vacuum. The polymer was transferred to a ceramic boat in the glove box, and placed in a silica tube with an arrangement of taps to allow flushing of the hoses before the sample was exposed to the gas flow. The sample was then fired under flowing ammonia (Air Products anhydrous grade, dried with 3 Å molecular sieves) at 500, 600, 700 or 800 °C for 2h.

The FTIR spectra of the polymeric precursor (Fig. S1) showed strong, broad peaks at 3215 (v_{NH}) and 640 cm⁻¹ (v_{MN}). Low intensity peaks at 3030-2760 (v_{CH}), 1609 (δ_{NH2}) and 1263 cm⁻¹ (v_{CN}) were also observed. The polymer was expected to contain bridging NH groups due to condensation of amide groups formed via transamination by ammonia with removal of dimethylamide groups from the Ti(NMe₂)₄ precursor. These data show that some residual organic substituents are still also present in the polymer.



Fig. S1 IR spectrum of the polymeric precursor obtained by reacting Ta(NMe₂)₅ with NH₃ in THF solution.

¹ D. V. Baxter, M. H. Chisholm, G. J. Gama, V. F. DiStasi, A. L. Hector and I. P. Parkin, *Chem. Mater.*, 1996, 8, 1222-1228.

Thermogravimetric analysis (TGA) was carried out in Mettler Toledo TGA/SDTA85le under flowing nitrogen (50 ml/min, Air Products BiP grade) up to 800 °C with a ramp rate of 10 °C/min. The instrument is housed in a glove box to allow handling of the air sensitive materials. The TGA trace of the polymer precursor (Fig. S2) shows a mass loss step at around 100-400 °C (~20%) and a further mass loss from around 700 °C. Previous work with TGA-MS showed that loss of amine and ammonia due to further condensation reactions is observed at lower temperatures.¹ Above 700 °C loss of N₂ from crystalline Ta₃N₅ is observed, though ammonia stabilises this material up to around 900 °C.² TGA of the samples heated to 600, 700 or 800 °C show very little mass loss at lower temperatures (Fig S3), suggesting that most amide groups have been decomposed at all these temperatures. The sample obtained at 500 °C shows ~0.2% mass loss at 300 to 500 °C due to decomposition of residual amide/imide groups, though these are insufficient in number for the hydrogen to be detected in the combustion analysis. All samples show mass loss above ~ 750 °C due to nitrogen loss.



Fig. S2 TGA trace in nitrogen of the polymeric precursor obtained by reacting Ta(NMe₂)₅ with NH₃ in THF solution.

² S. J. Henderson and A. L. Hector, J. Solid State Chem., 2006, **179**, 3518-3524.



Fig. S3 TGA traces in nitrogen of samples previously annealed in ammonia at the temperatures shown.

Phase pure orthorhombic Ta_3N_5 was obtained when the polymeric precursor was fired at 800 °C. Rietveld refinement of the PXD data for this sample (Fig S4) revealed a good fit to the known orthorhombic Ta_3N_5 structure with similar lattice parameters to those reported in the literature.²



Fig. S4 Fit to the PXD data ($\lambda = 1.5406$ Å) for the phase pure Ta₃N₅ obtained by pyrolysis of polymeric tantalum precursor at 800 °C. Crosses mark the data points, upper continuous line the calculated profile and lower continuous line the difference, tick marks are the allowed reflection positions of orthorhombic Ta₃N₅. Space group *Cmcm*, *a* = 3.896(33), *b* = 10.216(11) and *c* = 10.284(9) Å, R_{wp} = 16.5%, R_p = 11.6%.

TEM images showed homogeneous distributions of approximately isotropic particles of sizes ~50 nm, with some degree of agglomeration (Fig. S5). The similarity in morphology between samples is consistent with the previous observation that tantalum nitride does not undergo significant interparticular sintering at these



Fig. S5 TEM image of tantalum nitride samples produced by heating the polymeric precursor in ammonia at 500 (top) and 800 (bottom) °C.

Before laser heating the tantalum nitride sample produced by firing at 500 °C was studied during compression by Raman spectroscopy and XRD. No obvious features could be distinguished in the Raman spectra (Fig. S6). The steep rise above 100 cm⁻¹ is partly due to the spectral cut-off from the notch filter used in the Raman instrument. Above this value the spectrum of the amorphous material is relatively flat although broad weak features may be present near 250 cm⁻¹ and 400 cm⁻¹. The spectrum of the crystalline compound after laser heating exhibits only a monotonically decreasing background with no sharp phonon features in evidence. This would be consistent with a highly reflective sample as expected from the prediction of metallic behaviour for the U_3Se_5 structured phase.³

The XRD patterns are shown in Fig. S7. Interestingly, the broad feature at 9.0° moves to higher d-spacing initially on compression, before steadily moving to lower d-spacing after about 5 GPa. This behaviour is shown in Fig. S8 where it is also compared with that of the TaN 110 reflection calculated from the equation of state of TaN.⁴ Its position decreases more rapidly than the TaN peak, suggesting that the amorphous tantalum nitride is more compressible than TaN.

³ P. Kroll, T. Schroter and M. Peters, *Angew. Chem. Intl. Ed.*, 2005, 44, 4249-4254.



Fig. S6 Raman spectra of amorphous tantalum nitride produced at 500 °C (bottom) and the U_3Te_5/U_3Se_5 mixture produced by laser heating at 22 GPa (bottom).



Fig. S7 XRD patterns ($\lambda = 0.411$ Å) of amorphous tantalum nitride produced at 500 °C during compression to 26.4 GPa. The small peaks marked with asterisks are due to the rhenium gasket material.



Fig. S8 Variation in the position of the broad feature observed in the XRD patterns of tantalum nitride produced at 500 $^{\circ}$ C during compression to 26.4 GPa (black) and a comparison with the movement of the ϵ -TaN 110 reflection calculated from the equation of state (red).⁴

Structure refinement employed both the U_3Se_5 and U_3Te_5 structure types with fixed atom positions. Key structural parameters from this refinement are given in Tables S1-S2.

Table S1 Atom positions for Ta₃N₅ with the U₃Se₅ structure type (*Pnma*, a = 8.802(3), b = 6.044(4) and c = 5.492(3) Å).

Atom	Х	У	Z	U_{ISO} / Å ²
Ta1	0.322	0.999	0.473	0.025
Ta2	0.49	0.25	0.926	0.025
N1	0.592	0.456	0.169	0.025
N2	0.718	0.25	0.808	0.025
N3	0.499	0.25	0.541	0.025
N4	0.313	0.25	0.167	0.025

⁴ E. Soignard, O. Shebanova and P. F. McMillan, *Phys. Rev. B*, 2007, **75**, 014104.

Table S2 Atom positions for the U₃Te₅ structure used to model the second Ta₃N₅ phase a= 9.944(2), b= 2.691(6) and c= 9.015(6) Å).

Atom	X	У	Z	U _{ISO} / Å ²
Tal	0.1280	0.2500	0.4088	0.025
Ta2	0.3614	0.2500	0.5680	0.025
Ta3	0.3817	0.2500	0.2519	0.025
N1	0.0254	0.2500	0.6105	0.025
N2	0.0692	0.2500	0.2002	0.025
N3	0.2640	0.2500	0.7760	0.025
N4	0.2845	0.2500	0.0480	0.025
N5	0.5725	0.2500	0.5797	0.025

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As part of the fitting process a number of other models were also tried (Fig. S10) using the main alternative phase descriptions that could be expected based on current knowledge of the Ta-N system and Kroll's structure predictions.



 U_3Se_5 -type Ta₃N₅ only: $R_{wp} = 27.5\%$, $R_p = 21.7\%$

Other parameters as quoted for the U_3Se_5 -type plus U_3Te_5 -type fit as described above

U₃Se₅-type plus Ta₃N₅-type (Cmcm) Ta₃N₅: $R_{wp} = 81.1\%$, $R_p = 43.9\%$

Lattice parameters for Ta_3N_5 -type phase taken as 3.810, 9.80 and 9.850 Å as determined by ourselves (K. Woodhead, PhD thesis, University College London, 2013).

U₃Se₅-type plus Sm₂SnS₅-type Ta₃N₅: $R_{wp} = 38.6\%$, $R_p = 29.6\%$ a = 8.804 (5), b = 6.012(4) and c = 3.1231(4) Å

U₃Se₅-type Ta₃N₅ plus ϵ -TaN: R_{wp} = 37.0%, R_p = 27.5%

 ϵ -TaN (P-62m) unit cell parameters at 22 GPa estimated at a = 5.090 and c = 2.860 Å from the volume-pressure relationship in Soignard *et al.*⁴

