

Synthesis and characterization of a binary noble metal nitride

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There has been considerable interest in the synthesis of new nitrides because of their technological and fundamental importance^{1,2}.

Although numerous metals react with nitrogen there are no known binary nitrides of the noble metals. We report the discovery and characterization of platinum nitride (PtN), the first binary nitride of the noble metals group. This compound can be formed above 45–50 GPa and temperatures exceeding 2,000 K, and is stable after quenching to room pressure and temperature. It is characterized by a very high Raman-scattering cross-section with easily observed second- and third-order Raman bands. Synchrotron X-ray diffraction shows that the new phase is cubic with a remarkably high bulk modulus of 372(±5) GPa.

Owing to it having one of the strongest covalent bonds, nitrogen is very stable and inert under normal conditions. Yet nitrogen reacts with selected elements, forming compounds with a variety of intriguing properties. Some of the nitrides (mostly of group III and IV elements) produced by various methods are widely used as optoelectronic materials for example, light-emitting diodes and semiconducting lasers. Among the group-III elements that form nitrides, AlN and GaN, for example, crystallize in the hexagonal wurtzite structure, transforming to the face-centred-cubic (f.c.c.) at around 20 GPa and 50 GPa for AlN and GaN (refs 3,4), respectively. The group-IV elements form nitrides all having the cubic spinel structure: γ -M₃N₄ (where M = Si, Ge, Sn)^{5–8}. Theoretical studies of nitrides are also numerous, covering the topics of superconductivity⁹, optoelectronic^{10,11}, physical and structural properties^{10,12,13}. Another important group of these materials is the transition metal nitrides mostly known for their superconducting properties^{14–18}.

Most transition metals form nitrides at high temperatures and at either ambient or high pressure (for example, ZrN, VN, MoN). Groups for which there are no known binary nitride compounds are the scandium, manganese and copper families of elements¹⁹. The nickel and copper groups consist of metals all having f.c.c. structures stable in a wide pressure–temperature range²⁰. Because of their structural simplicity and stability, most of the metals from these groups are used as pressure

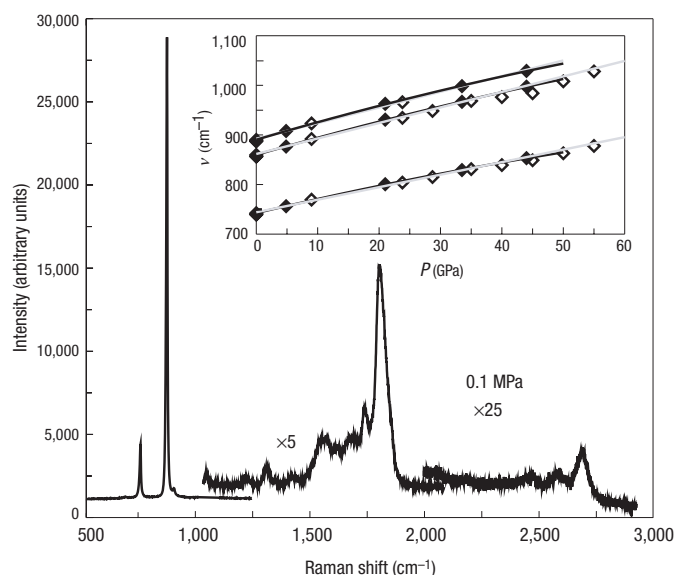


Figure 1 Representative Raman spectra (with second and third order peaks) of PtN. Measurements were done at 0.1 MPa and 300 K after quenching from 55 GPa. Inset: Pressure shifts of the first-order Raman bands of PtN. Open and filled diamonds represent different experimental runs. Solid lines are guides to the eye only.

standards in diamond-anvil-cell experiments, with platinum probably being the most often used (for example, ref. 21). Platinum forms simple binary compounds with halogens (for example, PtF₄, PtI₂); oxides and chalcogenides (for example, PtO, PtS) but it is not known to form nitrides¹⁹; among Ni, Pd and Pt only nickel²² has a nitride Ni₃N.

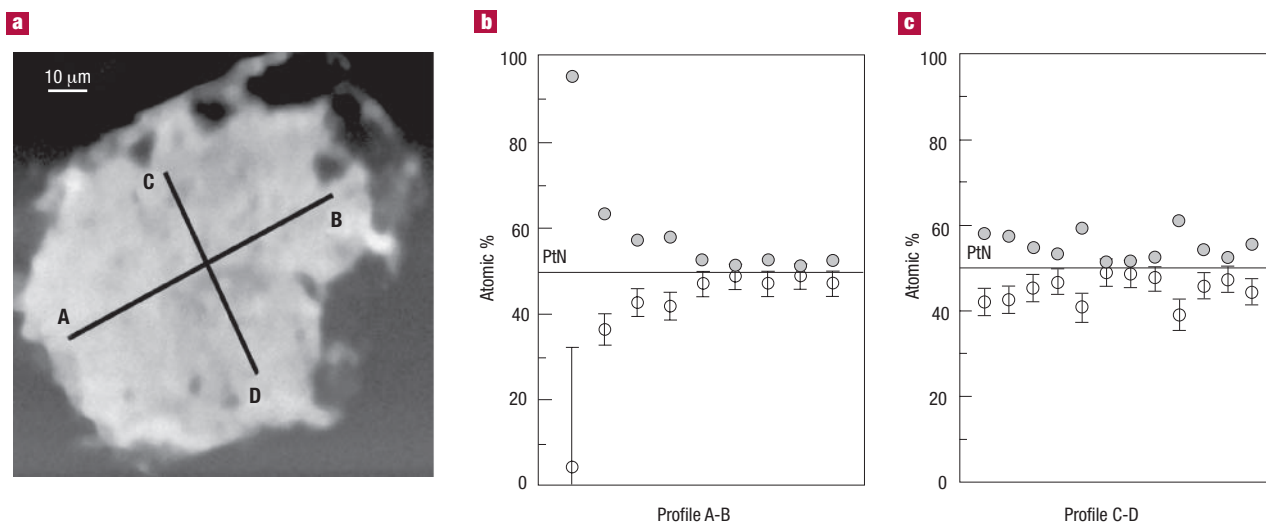


Figure 2 Chemical analysis of a reacted sample. **a**, Back-scattered electron image of an unloaded sample. **b,c**, Compositional profiles of the sample analysed by electron probe. Open circles: N content; closed circles: Pt content (the error bar on Pt is 0.55%).

There are number of ways to synthesise metal nitrides at ambient pressures. Synthesis can be done by chemical treatment at high temperature (>800 K), by laser irradiation or even mechanically by plastic deformation of the surface²³. Here we present the synthesis of a new nitride at pressures up to 50 GPa, using laser-heated diamond-anvil-cell techniques. This is one of the highest pressures at which synthesis has been carried out with complete recovery of the product to ambient conditions.

The reaction was first observed in Raman measurements following laser heating of samples at 2,000 K and at pressures above 45 GPa (Fig. 1). At lower pressures, after numerous heatings, the transformation to the nitride phase was never observed, whereas above 45–50 GPa the transition proceeds rapidly. The temperature of the transformation did not depend on the pressure within the investigated pressure range (45–60 GPa). Given that N₂ is often used as a pressure medium, and Pt used as a laser absorber in diamond-anvil-cell experiments, it is somewhat surprising that the reaction has not been reported previously. In fact, chemical reaction between sample and pressure media could be responsible for some of the inconsistencies found in laser-heated diamond-cell experiments²⁴. Previously, only reactions forming small molecules containing Pt and N in the gas phase have been reported (diatomic PtN by sputtering²⁵ and PtN, PtN₂ and (PtN)₂ by laser ablation²⁶).

The Raman spectrum is striking, with strong longitudinal optic (LO) mode and weaker transverse optic (TO) mode. Overall it is similar to that of cubic GaN and InN though the peaks are shifted in frequency as expected from mass effects^{27,28}. On the other hand, the spectrum is much more intense, with both second- and third-order scattering also observed (Fig. 1). The evolution of the Raman modes with pressure is also shown. The frequencies of the modes increase with pressure almost linearly, and the intensities of the bands remain quite strong even at the highest pressures. The mode Grüneisen parameter for LO mode is 1.35, for the highest frequency weak peak 1.31 and for TO it is 1.26.

After decompression, samples were recovered at ambient conditions and analysed by electron microprobe. Compositional profiles (Fig. 2) show that the Pt/N ratio is close to 1:1 but with some variations, that is, PtN_{1-x}, with $x < 0.05$. Pure platinum remains on the borders of the sample and also to lesser degree in the bulk. The micro-

Raman spectra measured across all PtN grains studied are identical, (laser spot ~5 μm), consistent with essentially no variation in stoichiometry. Moreover, the strength and width of the Raman fundamental bands are indicative of well-crystallized and highly ordered structure. The electron microprobe and Raman measurements probe mainly the surface (for example, ~1 μm for the microprobe at 5 kV); that these measurements are representative of the bulk is consistent with the X-ray diffraction data discussed below. All microprobes indicate either pure PtN or PtN plus unreacted Pt, although it is possible that in unreacted zones some nitrogen is dissolved in defects.

Synchrotron X-ray diffraction data were collected from two samples between ambient and 28 GPa (see Fig. 3). Two-dimensional diffraction patterns were angularly integrated with the Fit-2D program²⁹. The lattice parameters of both Pt and PtN phases were refined using the GSAS program package³⁰. In the first loading, after formation of PtN was confirmed by Raman scattering, X-ray data were collected at 28 GPa with the original nitrogen as the pressure-transmitting media. In the second run, the sample was recovered and reloaded with helium as the medium. All patterns at different pressure are consistent (see Fig. 3) and PtN can be indexed as f.c.c. ($a = 4.8041(2)$ Å at 0.1 MPa) at all pressures (for the full list of PtN d -spacings at different pressures see Supplementary Information). Although the Rietveld refinement is complicated by the strong Pt signal, the refinement agrees with the non-centrosymmetric space group $F\bar{4}3m$, to which the zinc-blende structure belongs, as well as the rock-salt structure ($Fm\bar{3}m$); the large mass difference between Pt and N makes it impossible to distinguish between these two structures from the diffraction intensities. Interestingly, the cooperite (PtS) structure has a Pt sublattice based on f.c.c., but it is tetragonal and the sublattice highly distorted ($ca \approx \sqrt{3}$ versus $ca = \sqrt{2}$ for ideal f.c.c.). The rock-salt structure does not have a first-order Raman spectrum and can therefore be ruled out. The zinc-blende structure has two Raman active peaks, consistent with the two strong first-order bands observed (see Fig. 1). A weak third Raman peak and even weaker additional peaks not shown in the figure are also evident; also ambient pressure X-ray diffraction patterns display two faint additional rings (see charge-coupled device image at 0.1 MPa in Fig. 3), whose texture differs from both Pt and PtN rings.

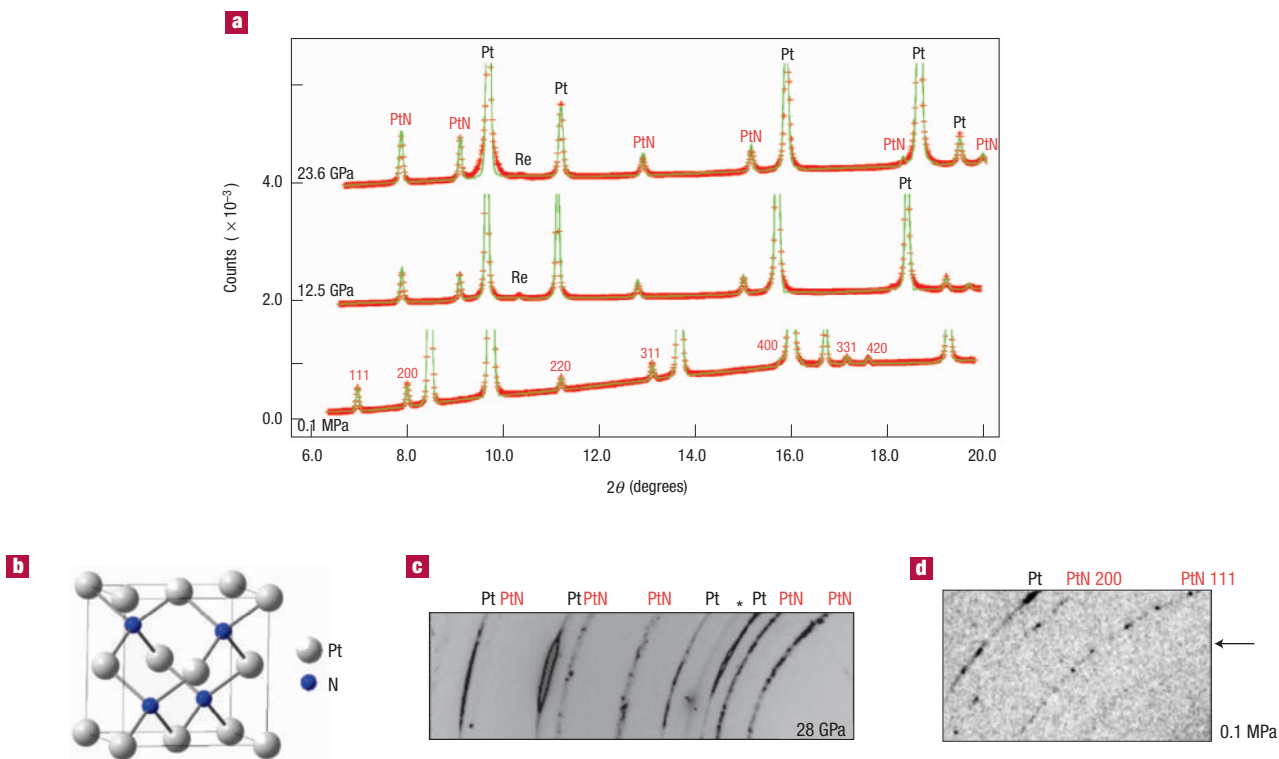


Figure 3 *In situ* X-ray diffraction data. **a**, X-ray spectra of PtN taken at different pressures. At ambient pressure the spectrum was taken with wavelength $\lambda = 0.3311 \text{ \AA}$ and others with $\lambda = 0.3738 \text{ \AA}$. Red crosses: data; green line: GSAS fit. **b**, Zinc-blende structure of PtN. **c**, Section of the CCD image at 28 GPa showing the powder-like texture; the asterisk indicates a rhenium diffraction ring. **d**, Detail of the inner section of the charged-coupled device image (shown in **c**) at ambient pressure with the arrow pointing at one of the two weak rings in addition to Pt and PtN signal.

The extra peaks in the Raman and X-ray diffraction profiles can be attributed to residual non-stoichiometric material distributed throughout the sample. However, the diffraction and spectroscopic data indicate that the bulk of the samples have same cubic structure. Crystallizing in the zinc-blende type PtN is therefore isostructural with high-pressure group-III nitrides as well as with most mononitrides at ambient pressure.

The evolution of the volume with pressure was fitted with a Birch–Murnaghan equation of state. The zero-pressure bulk modulus K_0 of PtN is about 100 GPa higher than pure Pt: $K_0 = 372(\pm 5)$ GPa with K'_0 fixed at 4 (or $K_0 = 354(\pm 5)$ GPa with the pressure derivative $K'_0 = K'_{0,\text{Pt}} = 5.26$). In both cases, the fitted volume at ambient conditions is $V_0 = 110.81(\pm 3)$, that is, $a = 4.8032(\pm 5) \text{ \AA}$. The K_0 of PtN is comparable to that of cubic-BN (ref. 31) ($372(\pm 5)$ and 379 GPa, respectively) a known superhard material. Figure 4 also shows that PtN is initially denser than $\text{Pt} + \frac{1}{2}\text{N}_2$, indicating that the reaction is pressure driven. However, the molar volume of PtN is larger than that of $\text{Pt} + \frac{1}{2}\text{N}_2$ above ~ 12 GPa, which indicates that PtN should break down or transform at higher pressures. The Pt cell parameter is systematically slightly smaller than is predicted by its equation of state²¹, ($< 0.2\%$, see Supplementary Information). K_0 of Pt determined in our experiments after the transformation took place is 20 GPa higher than pure Pt. These observations could be an additional indication that some N is dissolved in Pt (Fig. 4).

The high bulk modulus of PtN is a very interesting result. Theoretical calculations for transition metals nitrides³² indicate that in general if the bulk modulus of the pure metal is large it will be comparable for the corresponding nitride. The bulk modulus of PtN is

about 100 GPa higher than that of the pure Pt. This enhancement probably arises from a strong directional platinum–nitrogen covalent bond with orbitals being close to half-filled³². All PtN samples are lustrous and darker than pure platinum in reflected white light and totally opaque in transmitted light. Using a magnetic-susceptibility technique³³, we looked for the superconducting transition down to 2 K. The visual appearance and the absence of the superconducting signal suggest that PtN is either a poor metal or a semiconductor with a small bandgap, which is different to the most of the other transition metal nitrides known to be superconductors for example, VN, NbN.

Given the very high intensity of the Raman peaks and their systematic pressure dependence, the Raman spectrum can be used to calibrate the pressure. The relatively low pressure of the formation of the compound means that it can be reached with diamonds having a culet size of about 400 μm , which leaves about 200 μm for the sample chamber. By using fine platinum powder, one can produce enough material to be later used as calibrant in a diamond anvil. In fact, in one of our runs the amount of PtN powder recovered was enough to use in several diamond-cell experiments. Indeed, PtN might provide an alternative to the standard ruby powder (particularly at pressures below 100 GPa), as its Raman signal does not significantly decrease with pressure. The precision of the measurement would be much higher due to the small width of the Raman peaks; the bands stay narrow even at the highest pressures reached in this study. Also, it should be noted that the use of PtN as a pressure calibrant is appealing because one can simultaneously do X-ray and optical studies for the cross reference; indeed, there are not many compounds that have easily detectable Raman and diffraction signals. The very intense Raman signal of PtN

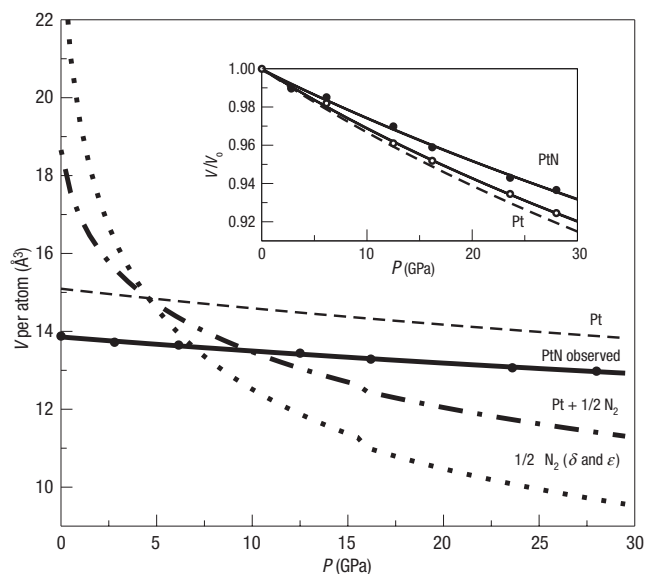


Figure 4 Analysis of the equation of state. Volume per atom for the observed PtN compared with the volume of pure Pt (ref. 21) and Pt + $\frac{1}{2}$ N₂; for N₂, equation of state of its δ and ϵ phases ref. 34) were used. Inset: Relative volume of PtN (solid circles) and Pt (open circles) as observed during our experiments. Solid curves: third-order Birch–Murnaghan fit of the pressure–volume data of PtN and Pt in these experiments; dashed curve: equation of state of pure platinum²¹.

can also be used as temperature calibrant in diamond-anvil cells. By measuring Stokes and anti-Stokes components of the Raman signal at the same time (the anti-Stokes Raman is easily observed even at room temperature with a collection time of one second) one can readily calculate the temperature of the sample *in situ*; that is, with laser heating we were able to measure the temperature of the sample from the Raman signal between 300 and 600 K, temperatures not accessible by spectral radiometry. It also showed that at lower pressures (~ 10 GPa), PtN breaks down on heating at about 450–500 K and the temperature of the back transformation increases with pressure.

In conclusion, using diamond-anvil-cell techniques we have synthesised and characterized a noble metal mono-nitride having a very high bulk modulus and remarkable Raman-scattering cross-section. Moreover, the material can be recovered at ambient conditions. Our results strongly suggest that it will be possible to synthesise other novel nitrides with transition metals, such as those in the nickel and copper groups (for example, Au or Ag) having potentially intriguing electronic properties. The results have important implications for high-pressure experiments and technology, for synthesis of superhard materials, and should stimulate further theoretical studies.

METHODS

Our experiments were conducted in symmetrical piston–cylinder diamond-anvil cells. Pure (>99.95%) platinum foil or powder was loaded in a 100–200 μm diameter hole of a rhenium gasket together with nitrogen gas. To determine the pressure, we used *in situ* fluorescence measurements of ruby chips loaded in the sample chamber. Pressure was measured before and after heating and did not change appreciably. For Raman spectroscopy, we used various argon-ion laser lines as excitation sources. The temperatures were measured to within ± 150 K by thermal radiation. Diffraction data were collected at beamline 16-ID-B (HPCAT) at the Advanced Photon Source, Argonne National Laboratory, Illinois, USA. Focused, monochromatic beams of different wavelengths were used, and the data were recorded on a MAR CCD calibrated with a CeO standard. The electron microprobe analysis (JEOL 8800L) was done with a current of 50 nA and 5 kV of accelerating voltage.

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Competing financial interests

The authors declare that they have no competing financial interests.