Synthesis and Characterization
Synthesis and Characterization of Nitrides of Iridium and Palladium

Jonathan Crowhurst¹, Alexander Goncharov², Babak Sadigh¹, Joseph Zaug¹, Yue Meng³, and Vitali Prakapenka⁴

¹Lawrence Livermore National Laboratory, 7000 E Avenue, Livermore, CA, 94551
²Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC, 20015
³HPCAT, Advanced Photon Source, Argonne National Laboratory, Argonne, IL, 60439
⁴GSECARS, Advanced Photon Source, Argonne National Laboratory, Argonne, IL, 60439

ABSTRACT

We describe the synthesis of nitrides of iridium and palladium using the laser-heated diamond anvil cell. We have used the in-situ techniques of x-ray powder diffraction and Raman scattering to characterize these compounds and have compared our experimental findings where possible to the results of first-principles theoretical calculations. We suggest that palladium nitride is isostructural with pyrite while iridium nitride has a monoclinic symmetry and may be isostructural with baddeleyite.

INTRODUCTION

Metallic and ceramic nitrides are of great technological and fundamental importance [1-6]. Traditional applications have taken advantage of the hard and refractory nature of many of these compounds, but numerous more recent applications are based on their optical, electronic, and magnetic properties. Of the transition metals most are known to form compounds with nitrogen but it is only recently that solid "bulk" nitrides (as opposed to small individual molecules) of Au [7], Pt [1,8,9], Ir [9-11], Os [11], and Pd (present work) have been reported. Synthesis techniques have included nitrogen ion irradiation (Au [7]), reactive laser ablation (Pt [8]), and the use of the laser-heated diamond anvil cell (Pt [1,9], Ir [1,9,11], Os [11], Pd). The anvil cell has also been used to synthesize novel phases of known nitrides e.g. silicon, zirconium and hafnium [12-13].

EXPERIMENT AND THEORY

The relevant metal was placed into the DAC cavity either in the form of thin squares (approximately 30 X 10 microns) or fine powder. Raman scattering was used to determine when a reaction had occurred. Our combined laser-heating and Raman system which we used to synthesize all of our samples has been described elsewhere [14]. In the case of iridium, nitrogen was loaded into the DAC cryogenically for all synthesis experiments. For palladium, several cryogenic loadings were also performed but for one synthesis, nitrogen was loaded under high pressure at room temperature. It is well known that the latter method permits much higher reactant purity [15] while "open vessel" cryogenic loading may well be expected to result in impurities such as oxygen and water. However, our Raman spectra for iridium nitride was
essentially identical to that reported by Young et al. [11] who we believe employed high-pressure gas loading in their investigations. Since palladium nitride had not been previously reported we thought it necessary to demonstrate at least that the Raman spectra were the same for both loading procedures.

For the XRD measurements the DACs were equipped with tungsten carbide seats of the Boehler-Almax design [16] or with conventional seats having a slot aperture of similar angular extent in one direction. XRD measurements were performed with focused (typical spot dimension was 10 by 14 μm) monochromatic synchrotron radiation in the 28-34 keV range at the IDB HPCAT and ID13 GSECARS beam lines of the Advanced Photon Source (ANL). XRD measurements were also performed at the 12.2.2 beam line of the Advanced Light Source (LBL) (spot dimension of ~ 10 μm diameter and energy 30 keV).

The thermodynamic stability of candidate structures as a function of pressure was determined by performing density functional calculations within the generalized gradient approximation (GGA) in the PW91 parametrization [17]. We used the VASP package that implements the projector augmented wave (PAW) method [18,19]. Formation energies at ambient pressure as well as at synthesis conditions were obtained by subtracting the chemical potentials of the constituents in their pure phases from that of the proposed structure. Further details may be found in Ref. 9.

DISCUSSION

As reported in Ref. 9 synthesis conditions for iridium nitride, IrN₂, were approximately 48 GPa and 1600 K consistent with Ref. 11 and similar to those for platinum nitride, PtN₂ [1,9]. Palladium nitride, however, forms at significantly higher pressures (above 58 GPa) but at much lower temperatures (well below 1000 K - where measurements based on thermal emission were unreliable). Furthermore, although both iridium and platinum nitride are recoverable to ambient conditions, palladium nitride probably is not and most likely decomposes at pressures below ~13 GPa. In fact the laser excitation used for the Raman measurements was sufficient to decompose the compound even at 20 GPa. The lower value was obtained by noting the pressure

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Measured Raman spectra of iridium nitride (a), and palladium nitride (b), at 0 GPa and 60 GPa, respectively.
at which the XRD pattern disappeared. We thus could not determine the ratio of metal to nitrogen atoms using either of the techniques of electron microprobe or x-ray photoelectron spectroscopy as was done for platinum and iridium nitride [1,9]. Raman spectra for both compounds were distinctive and reproducible (Fig. 1). The spectrum of IrN₂ contained at least 11 modes. That of palladium nitride was simpler. It contained two intense modes and around the base of the higher frequency mode there also appeared to be at least two much weaker modes.

![X-ray diffraction pattern of iridium nitride and of unreacted iridium at 0 GPa. Bars represent the positions and intensities of calculated x-ray powder diffraction patterns for pure Ir (fcc) and for IrN₂ with the structure that we propose in the text.](image)

**Figure 2.** X-ray diffraction pattern of iridium nitride and of unreacted iridium at 0 GPa. Bars represent the positions and intensities of calculated x-ray powder diffraction patterns for pure Ir (fcc) and for IrN₂ with the structure that we propose in the text.

This difference between the two compounds was also mirrored in the degree of complexity of the respective XRD patterns (Figs. 2 and 3). Although the XRD measurements were not sensitive to the relative positions of the nitrogen atoms in the compounds they were used to precisely determine the lattice parameters and symmetries of the sub-lattices of the metal atoms. We found that for palladium nitride this sub-lattice had a face centered cubic (fcc) symmetry but for iridium nitride it had a monoclinic symmetry. We note that a monoclinic structure for IrN₂ is not consistent with the rhombohedral or hexagonal structure previously reported [11]. A structure which is consistent with the available experimental data is that of baddeleyite (ZrO₂). Our theoretical calculations show that it has a negative energy of formation at 50 GPa and in any case has a lower energy than for the other proposed structures. An electronic density-of-states
Two theta (degree)

Figure 3. X-ray diffraction pattern of palladium nitride and of unreacted nitrogen and palladium at 47 GPa. Bars represent the positions and intensities of calculated x-ray powder diffraction patterns for Pd (fcc) and palladium nitride (black bars) assuming a pyrite structure.

calculation shows that the material has a much smaller band gap than that of platinum nitride but nevertheless to be non-metallic, which is possibly consistent with the stronger Raman spectrum of PtN$_2$. The baddeleyite structure has 18 Raman active modes whereas we only clearly observe 11. According to our calculations, however, at least three of these in IrN$_2$ have frequencies that are so low as to make them unobservable in our experimental Raman spectra. Figure 3 compares experimentally measured pressure dependences of mode frequencies with values calculated at 0 and 50 GPa assuming a baddeleyite structure. Overall agreement is good. Several modes are very close in frequency and this together with different relative intensities may account for the additional 4 missing modes.

Although we are hampered by not knowing the stoichiometry of palladium nitride we may still suggest a reasonable structure for this compound. In terms of number of modes and intensity ratios the Raman spectrum of palladium nitride is comparable to that of pyrite PtN$_2$ [9,20]. Furthermore, the fcc sub-lattice determined from XRD measurements is consistent with a
pyrite structure. Also, theoretical calculations show that palladium nitride with the pyrite structure is very soft and is probably elastically unstable at 0 GPa [21], although it does become energetically favorable at high pressures according to our calculations.

**Figure 4.** Measured Raman mode frequencies of iridium nitride vs pressure. Also shown are calculated frequencies assuming the baddeleyite-type structure at 0 and 50 GPa.

**CONCLUSIONS**

We have proposed a new baddeleyite structure for IrN$_2$ iridium nitride. We have also synthesized the new compound palladium nitride whose stoichiometry is probably PdN$_2$ and which crystallizes in the pyrite structure. IrN$_2$ is recoverable to ambient conditions but PdN$_2$ is not. Bulk moduli, equation of state, and other properties of these compounds will be reported elsewhere. This work further demonstrates the utility of the diamond cell for synthesizing and characterizing novel compounds. If a means can be found to synthesize compounds such as IrN$_2$ and PtN$_2$ on a large scale (such as ion irradiation [7]) technological applications that take advantage of the properties of these materials may become feasible. We note that gold nitride while harder than gold and still electrically conductive [22], is also sensitive to x-ray and...
electron beam irradiation [23]. This has led Butenko et al [23] to suggest x-ray or electron beam lithography may be used to write patterns directly onto gold nitride. We suggest that the same may be true for the highly metastable compounds IrN2 and PtN2.

ACKNOWLEDGMENTS

JC gratefully acknowledges discussions with R. Yu, E. Gregoryanz, P. Kroll, and M. Somayazulu. JC and JZ also thank S. Caldwell for assistance with XRD measurements. Use of the HPCAT facility was supported by DOE-BES, DOE-NNSA (CDAC), NSF, DOD-TACOM, and the W.M. Keck Foundation. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-Eng-38. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098 at Lawrence Berkeley National Laboratory and the University of California, Berkeley, California. Work at LLNL was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

REFERENCES
