High-Pressure Synthesis and Characterization of Incompressible Titanium Pernitride

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Supporting Information

Transition metal nitrides represent an important class of materials exhibiting a wide variety of properties including high refractivity, \(^1\) superconductivity, \(^2\) and recently, electrocatalytic activity. \(^3,4\) Most transition metal nitrides exist with ratios of N:M \(\leq 1\) (M-metal) and they exhibit metallic properties. On the other hand, nitrogen-rich transition metal pernitrides, which can be synthesized at high pressures, exhibit superior properties as compared to the corresponding nitrides. \(^5-\)\(^9\)

In the recent past, there has been enormous attention to transition metal pernitrides after the successful synthesis of ultraincompressible PtN\(_2\) with a bulk modulus 372 GPa. \(^7\) The search for the other transition metal pernitrides led to the discovery of OsN\(_2\), \(^10\) IrN\(_2\), \(^10,11\) PdN\(_2\), \(^12\) RuN\(_2\), \(^12\) and RhN\(_2\). \(^13\) The structures of these materials contain pernitride (N\(_2\))\(^-\) units that are encapsulated in the metal lattice and are isoelectronic to peroxide ions (O\(_2\))\(^-\), also isoelectronic with molecular fluorine), hence the name pernitride. They exhibit three main types of crystal structures: PtN\(_2\) and PdN\(_2\) crystallize in the pyrite (cubic Pa\(_{3}\)) structure; \(^5,11\) IrN\(_2\) exhibits the arsenopyrite-type structure, while OsN\(_2\), RhN\(_2\), and RuN\(_2\) crystallize in the marcasite (orthorhombic Pnnm) \(^14-16\) structure. Although their space groups are different, most pernitrides can be characterized by nitrogen atoms octahedrally coordinating metal atoms to form MN\(_6\) octahedra that are interconnected in three dimensions through dinitrogen (N\(_2\)) bonds. Here, the covalent N–N interactions are of single bond nature, as indicated by strong first-order Raman modes near 1000 cm\(^{-1}\) (compare with hydrazine N\(_2\)H\(_4\)), as observed for nonmetallic samples. \(^5,10,17\) The N–N bond length in PtN\(_2\) and OsN\(_2\), is between 1.4 and 1.42 Å, which is close to the bond length of ultraincompressible, single-bonded polymeric nitrogen. \(^17\) Previous studies suggest that the extraordinary mechanical and electronic properties of transition metal pernitrides may originate from metal–nitrogen charge transfer and the nature of the N–N bonds. \(^18-20\) Thus, synthesis of new pernitrides and an understanding their bonding character is not only important from a fundamental perspective but also essential for realizing new materials with technological applications.

In this communication, we discuss the synthesis and characterization of titanium pernitride (TiN\(_2\)). This new nitride is incompressible with a bulk modulus in the range of 360–385 GPa and is expected to be the hardest among all Ti–N compounds. \(^21\) We have used \textit{ab initio} calculations based on density functional theory (DFT) \(^22,23\) to understand the crystal structure, thermodynamic properties, and bonding nature of TiN\(_2\). Although there were a few theoretical reports that predicted the crystal structure and properties of TiN\(_2\) before \(^21,24\) there was no prior experimental evidence to validate these predictions. Previous attempts of the synthesis of nitrogen-rich titanium nitrides was unsuccessful, possibly due to the choice of the starting materials and synthesis conditions. \(^25\)

TiN\(_2\) was synthesized using the laser-heated diamond anvil cell technique at 73(3) GPa and 2400(40) K. The starting materials consisted of a small (10 \(\times\) 15 \(\times\) 5 \(\mu\)m\(^3\)) flake of TiN loaded in the DAC that was surrounded by a dense N\(_2\) pressure transmitting medium. After compression, samples were heated using an infrared laser and then probed by X-ray diffraction (XRD) (see methods in Supporting Information). The X-ray diffraction pattern of the laser heated sample (Figure 1a) is dominated by Bragg peaks from solid molecular nitrogen that surrounded the original TiN sample on all sides and represented the majority of the sample chamber volume. Some of these peaks are consistent with the reported structure of \(\zeta\)-N\(_2\)\(^16,26,27\) however, the exact structure of N\(_2\) at these thermodynamic conditions is currently unresolved. Nevertheless, the N\(_2\) Bragg reflections are unambiguously identified by probing the sample volume containing only pure N\(_2\). In addition to these反射s, we also observed new sharp and well-resolved peaks in the pattern that can be easily indexed to a tetragonal unit cell (space group I\(_4/mcm\)) with lattice parameters of \(a = b = 4.092(1)\) Å and \(c = 4.974(1)\) Å at 73 GPa. These parameters are in excellent agreement with recent predictions of Yu et al. \(^23\) for the CuAl\(_2\)-type TiN\(_2\) structure and indicate the formation of this phase. This is in contrast to Kulkarni et al. \(^28\) who suggested the possibility for TiN\(_2\) with the orthorhombic P\(_nnm\) type structure.

On decompression, we found that this phase is recoverable to ambient conditions and remains mechanically stable in air. The phase determination of the recovered sample confirms the high pressure indexing and removes any uncertainties associated with overlapping \(\zeta\)-N\(_2\) peaks as all gaseous N\(_2\) was evacuated from the cell at 0 GPa. The TiN\(_2\) phase remains in the tetragonal I\(_4/mcm\) structure at ambient conditions with lattice parameters \(a = b = 4.334(1)\) Å and \(c = 5.294(2)\) Å. Apart from TiN\(_2\) and some unreacted TiN, we also observed diffraction lines from rhenium as the sample moved close to the gasket edge during decompression. Based on two-dimensional diffraction images (as shown in Figure S2), which show “spotty” Debye–Schererrer rings with strong

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The communication to the orientations of TiN2 grains which yield topography-stoichiometry of the sample in the heated region could be due whereas the nonheated area gives a ratio of 1:1. The variation in region gives stoichiometries varying between 1:2 and 1:2.5, the estimated atomic ratio between Ti and N in the heated nitrogen in this region as compared to the rest of the sample. areas, demonstrating the presence of a higher concentration of image shows strong contrast between the heated and unheated size to the synchrotron beam (i.e., is of polycrystalline nature with individual grains of comparable

The large volume dimension to texturing of the laser heated area, which indicates recrystallization due to chemical reaction of TiN with N2. The large volume difference between TiN and TiN2 (pink dotted line) at room temperature. Inset shows the pressure dependence of the lattice parameters a and c (solid symbols). The solid lines are the EoS fit to the experimental data. The green dotted line is the calculated EoS of TiN2 using PBEsol for the I4/mcm structure (V0 = 97.61 Å3, K0 = 328 GPa, K0′ = 4.0). The error values for the lattice parameters are smaller than the size of the symbols.

Figure 1. (a) X-ray diffraction patterns of laser heated TiN + N2 system. The black tick marks indicate the Miller indices of the tetragonal I4/mcm lattice. Optical micrograph shows the rhenium and sample at 73 GPa inside the diamond anvil cell. (b) Scanning electron microscopy image of the recovered sample. The laser heated spot is encircled. (c) The energy dispersive X-ray spectroscopy map of the recovered sample where the colors indicate relative concentrations of the various elements. The concentration of Ti and N at two different spots in the heated and unheated regions on the sample is listed in the table.

Figure 2. Experimental pressure—volume data of TiN2 (black circles) compared with the pressure—volume relation of the reactants, i.e., TiN + 1/2N2 (pink dotted line) at room temperature. Inset shows the pressure dependence of the lattice parameters a and c (solid symbols). The solid lines are the EoS fit to the experimental data. The green dotted line is the calculated EoS of TiN2 using PBEsol for the I4/mcm structure (V0 = 97.61 Å3, K0 = 328 GPa, K0′ = 4.0). The error values for the lattice parameters are smaller than the size of the symbols.

azimuthal variations in intensity, the as-synthesized TiN2 phase is of polycrystalline nature with individual grains of comparable size to the synchrotron beam (i.e., ~5 μm). It was therefore not possible to perform quantitative Rietveld refinements on integrated one-dimensional patterns to precisely determine atomic positions. Nevertheless, the integrated intensities of all observed reflections qualitatively correspond with predicted intensities (see Figure 1a) derived from the ab initio I4/mcm structural model using nitrogen atoms at 8h Wyckoff positions (x = 0.1124). Thus, the synthesis of I4/mcm TiN2 is confirmed through this qualitative intensity agreement and excellent quantitative agreement in unit cell symmetry and lattice parameters.

Scanning electron microscopy images obtained from the recovered sample (as shown in Figure 1b) show cracks leading to texturing of the laser heated area, which indicates recrystallization due to chemical reaction of TiN with N2. The large volume difference between TiN and TiN2 likely facilitates this cracking and texturing of the laser heated area. Energy dispersive spectroscopic (EDS) analysis of the recovered sample is shown in Figure 1c. The EDS layered image shows strong contrast between the heated and unheated areas, demonstrating the presence of a higher concentration of nitrogen in this region as compared to the rest of the sample. The estimated atomic ratio between Ti and N in the heated region gives stoichiometries varying between 1:2 and 1:2.5, whereas the nonheated area gives a ratio of 1:1. The variation in stoichiometry of the sample in the heated region could be due to the orientations of TiN2 grains which yield topography-related errors in EDS analysis. Nevertheless, the measured compositions in the heated and nonheated regions provide further confirmation for the formation of TiN2.

Further insights into the new phase can be gained by comparing its volume versus pressure data (P–V data) with that of the reactants (i.e., TiN + 1/2N2). The necessary thermodynamic condition for the pressure-induced chemical reaction is that the volume per atom of the products must be smaller than that of the reactant phases throughout the pressure range. It is evident from Figure 2 that the measured volume per atom of TiN2 is always smaller than that of TiN + 1/2N2. The huge volume difference (~11%) between the reactants and the product indicates that the reaction product is indeed a new compound (as opposed to a phase transition in TiN).

The P–V data were fitted using the third order Birch–Murnaghan equation of state (EoS) (as shown in Figure 2). The zero-pressure bulk modulus, K0 = 385(7) (with K0′ = 1.45(18)) obtained here is far higher than all other known phases in the Ti–N system.29 Also, the measured bulk modulus is close to that of c-BN (K0 = 382(3), K0′ = 4.46(15))28 indicating that tetragonal TiN2 is incompressible and could be a potential superhard material (a thermodynamic model suggests a hardness near 30 GPa23). It is to be noted that the refined value for K0′ is lower than that obtained for most materials. It is quite normal that the parameters K0 and K0′ correlate heavily while fitting the compression data using EoS fit.23 This means the data can be fitted almost equally well by decreasing the value of K0 and increasing the value of K0′ or vice versa. To better illustrate the extent of correlation between K0 and K0′ and to see the range of possible values for K0 and K0′, we have used 3σ, 2σ, and 1σ confidence ellipses in the parameter space of K0 and K0′ as shown in the Supporting Information (see Figure S3a). The K0′ value is less than 2 even at 99.73% confidence level. Correspondingly, K0 acquires values higher than 360 GPa. Looking at these confidence ellipses, we can unequivocally report that the bulk modulus of TiN2 is higher than 360 GPa.
The thermodynamic behavior of TiN$_2$ was investigated further via ab initio (DFT) calculations using different functionals (PBE, PBEsol, and LDA). The formation enthalpy of TiN$_2$ at 1 atm is 0.386 eV/atom, and it is also metastable with respect to disproportionation into TiN + N$_2$.

The calculated structural and EoS parameters are summarized in Table S1. The calculated bulk moduli are systematically lower than the estimated value from experiment, which was also observed for several other pernitride systems. The discrepancy here is the consequence of a monotonically increasing under-prediction of the experimental lattice parameters as pressure decreases from 73 GPa. Nevertheless, PBEsol showed the best agreement with experiment (Figure 2) with an average deviation of only $\pm 1.7\%$ over the entire pressure range.

The structure of TiN$_2$ is CuAl$_2$-type with 4 formula units per unit cell. It consists of layers of N$_2$ and Ti stacked along the $c$-axis. Unlike other metal pernitrides, which usually contain MN$_6$ (M-metal) octahedra, TiN$_2$ contains TiN$_6$ face-sharing tetragonal antiprisms stacked along the $c$-axis (as shown in Figure 3a). The neighboring antiprisms along the $a$ and $b$-axes are connected through N$_2$-dumbbells (see Figure 3b) and is analogous to the structure of SrS$_2$. The separation between two neighboring N$_2$-dumbbells along the $a$-axis is larger than that along the $c$-axis, and the dihedral angles between two neighboring N$_2$-dumbbells along $c$ and $a$-axes are 86.3° and 180.0°, respectively. This observation suggests that the nearest-neighbor N$_2$ dumbbells along the $c$-axis are oriented with respect to each other to minimize steric hindrance. Based on our ab initio calculations, the N−N bond distance at ambient pressure is found to be 1.383 Å and is comparable to the F−F bond length (1.42 Å) in molecular F$_2$ and the N−N bond length in pernitrides of some transition metals such as PtN$_2$ (1.41 Å) and OsN$_2$ (1.43 Å). This distance indicates that the N$_2$ dumbbells in TiN$_2$ exist as N$_2^{+}$ (pernitride ions with N−N single bonds). This is in contrast with N$_2^{2-}$ ions, observed for example in BaN$_2$, which exhibits N−N bond lengths of 1.23 Å. Further confirmation for N−N bonding character can be gained from the vibrational frequency of the dinitrogen units. Unfortunately, the Raman spectrum of TiN$_2$ collected using a low laser power shows no Raman signal (see Figure S4) likely due to the metallic nature of this phase, as predicted previously and consistent with the absence of Raman signal in other metallic pernitrides. However, the theoretically predicted N−N vibrational frequency is $\sim 1150$ cm$^{-1}$ which is higher than that of PtN$_2$ (860 cm$^{-1}$) and much lower than that of BaN$_2$ (1466 cm$^{-1}$). This confirms that the N−N bonds within TiN$_2$ are of single bond character and the bonding is slightly stronger as compared with PtN$_2$ as reflected in both bond length and vibrational frequency.

To gain deeper insights into the electronic properties and bonding features of TiN$_2$, we have performed electronic band structure calculations based on DFT using PBEsol. The orbital-resolved “fat-band” plot for TiN$_2$ at ambient pressure along high-symmetry directions is shown in Figure 3c. It is clear from this electronic band structure that TiN$_2$ is metallic and several bands are crossing the Fermi level ($E_F$), which is set to zero in the plot. The fat-bands show different atomic orbital contributions to the conduction bands and are comprised of mixed Ti-$d$ and N-$p$ states. Delocalized electrons at the top of the conduction bands that are responsible for metallicity originate from both Ti-$d$ and Ti-$d$/N-$p$ hybrid electrons. The complete picture of chemical bonding within TiN$_2$ is complex and clearly of mixed character. While formally metallic, the DOS at the Fermi level is low (1.8 states/eV/4f.u.) and a broad pseudogap is formed between occupied hybrid Ti-$d$/N-$p$ states (below $E_F$) and unoccupied states (above $E_F$) with predominately Ti-$d$ character. These features have been used as indicators of covalency in related materials. Covalent character between Ti and N is also indicated by the concurrence between bonding orbital character in Ti−N−pCOHP (projected Crystal Orbital Hamilton Population) analysis and by the presence of hybrid Ti-$d$/N-$p$ electrons between $-8.5$ eV up to $E_F$ in the partial DOS. As indicated by Yu et al. and verified here by -pCOHP analysis, the antibonding $1\pi_g^*$ orbitals (starting near $-2$ eV) are almost completely occupied at the top of the conduction band, and a portion of the metallic nature can be ascribed to these states being occupied at the Fermi level. As suggested by Wessel et al. for the case of PtN$_2$, charge transferred from Pt to N results in the filling of antibonding $1\pi_g^*$ states of N$_2$$^{2-}$. This filling serves to elongate the N−N bonds and, in conjunction with Coulomb repulsion, makes the system more resistant to external stress and results in high mechanical strength of the system. While there are differences in electronic and structural configurations, this mechanism is also at play for the case of TiN$_2$ although antibonding states are not completely filled and

![Figure 3. (a, b) crystal structure of $I4/mcm$ TiN$_2$ with N−N dumbbells; (c) fat-band plot of TiN$_2$ with Ti-$d$ and N-$p$ characteristics. The notation of the symmetry points is as follows: $Z$ (0, 0, 1/2); $A$ (1/2, 1/2, 1/2); $M$ (1/2, 1/2, 0); $\Gamma$ (0, 0, 0); $Z$ (0, 0, 1/2); $R$ (0, 1/2, 1/2); $X$ (0, 1/2, 0); and $\Gamma$ (0, 0, 0). (d) Total and partial density of states (DOS). (e) Projected Crystal Orbital Hamilton Population (-pCOHP) analysis of various bonds in TiN$_2$. The Fermi level ($E_F$) is indicated by gray dashed line.](image-url)
N–N bonds are somewhat shorter. Bader charge analysis indicates that 1.8 e\textsuperscript{−} are transferred from Ti to N\textsubscript{2} in contrast to 1.05 e\textsuperscript{−} for PtN\textsubscript{2} in the pyrite structure. Overall these results indicate that TiN\textsubscript{2} can be viewed as possessing more ionic/metalllic character than PtN\textsubscript{2} (covalent/ionic), although their mutual incompressibilities share similar origins. In summary, we have synthesized a new transition metal pernitride, TiN\textsubscript{2}, with tetragonal 14/mcm symmetry that exhibits a high bulk modulus. Based on our ab initio calculations, we tried to understand the bonding character and thereby the origin of high bulk modulus of TiN\textsubscript{2}. The results presented here have important implications in synthesis of new metal nitrides and the understanding their structure–property relationships. We hope that our findings will encourage further theoretical and experimental work.

**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is available on free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmat.6b00042.

Experimental methods, computational details, and additional figures/table (PDF)

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**Author Contributions**

V.S.B. and T.A.S. have performed the experiments and analyzed the data. D.Y.K. has performed the theoretical calculations. The manuscript was written with contributions from all authors.

**Notes**

The authors declare no competing financial interest.

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