How the search for a new semiconductor photocatalyst lead to the discovery of an ultraincompressible metal

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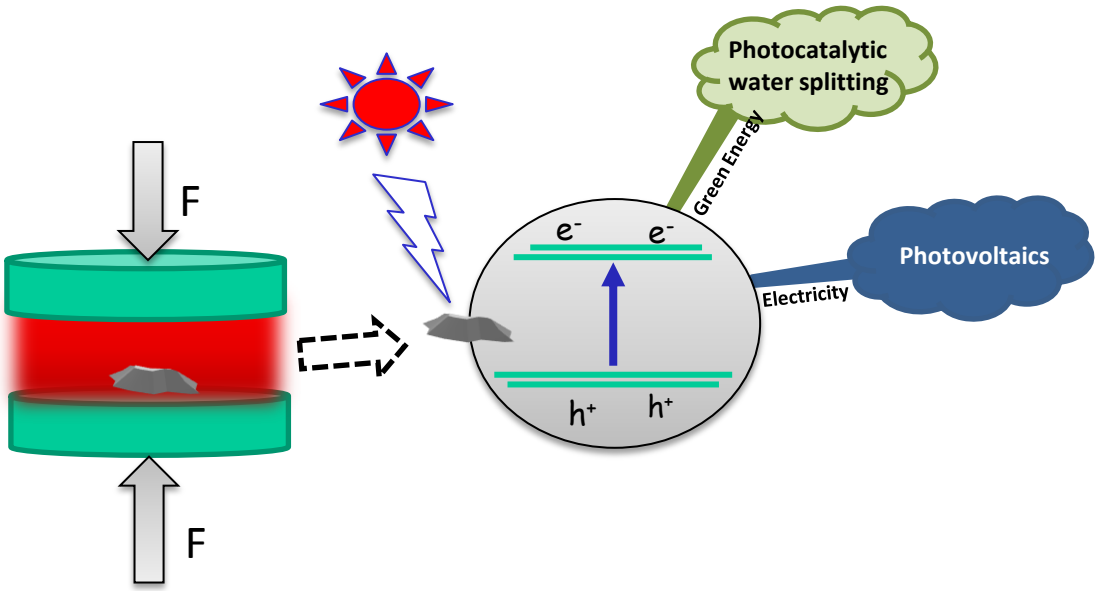
V. S. Bhadram, D. Y. Kim and T. A. Strobel, *Chem. Mater.* (accepted)

Semiconductors for solar energy harvesting applications

New Solar Materials Project

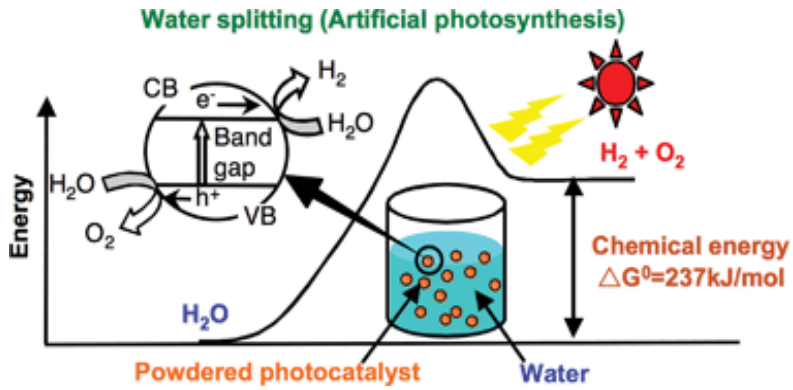
Synthesis of new materials using HPHT technique which can be used for solar light harvesting applications



Energy Frontier Research in Extreme Environments Center

Carnegie Institution for Science

Semiconductor Photocatalysts for Production of H_2 from water



Kudo et al, *Chem. Soc. Rev.*, 253, 209 (2009)

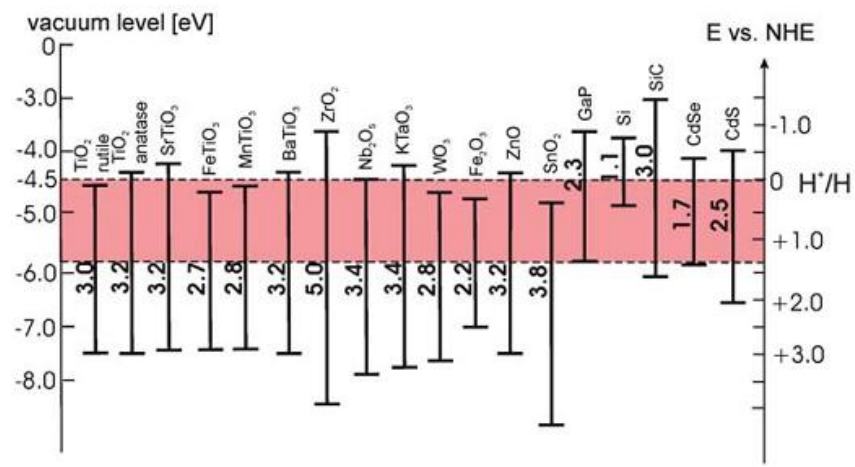
Requirements for a semiconductor photocatalyst

- ❑ Bandgap ≥ 1.23eV
- ❑ Band-edges straddle H_2O redox couple
- ❑ Absorption in the visible solar spectral region
- ❑ High carrier mobility
- ❑ stability towards photocorrosion

❑Stable metal oxide photocatalysts are not so efficient due to their bandgaps in the UV-region.

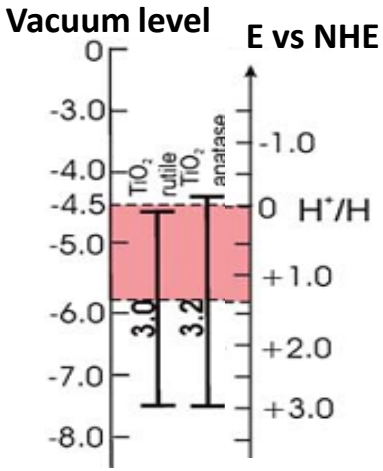
❑Discovering new semiconductor photocatalysts is essential for efficient production of H_2 through water splitting.

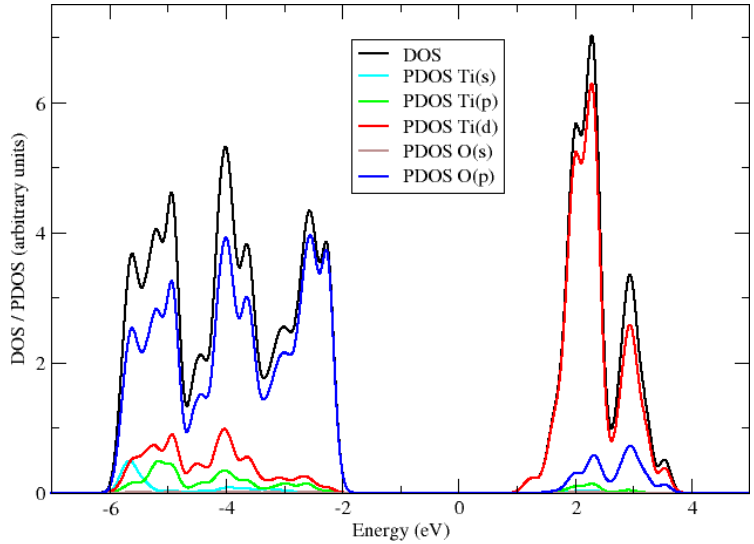
❑ Preferential doping can be used to tune the bandgaps of existing photocatalysts.



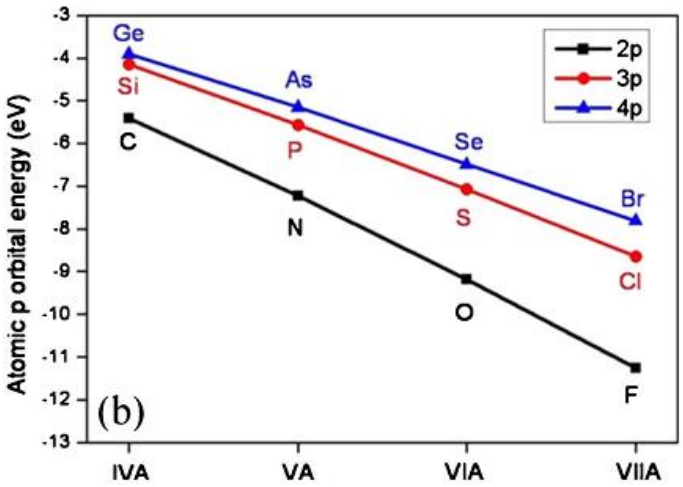
Batzill, *Energy Environ. Sci.*, 2011

The case of TiO_2





http://www.dftb-plus.info/fileadmin/DFTB-Plus/public/recipes/html/basics/bandstruct.html



Phys. Rev. B ,82, 045106 (2010)

For the up shift of VB edge; anions with p- orbital energies higher than O 2p.

e.g: N, C, S, P, Si, Se, As

Replacing 'O' with 'N'

TiO_2	$TiO_{2-x}N_x$	TiN_2
❑ Photocatalyst ❑ E_g = 3.0-3.2eV	❑ Photocatalyst ❑ E_g < 3.0eV	Doesn't exist

TiN_2

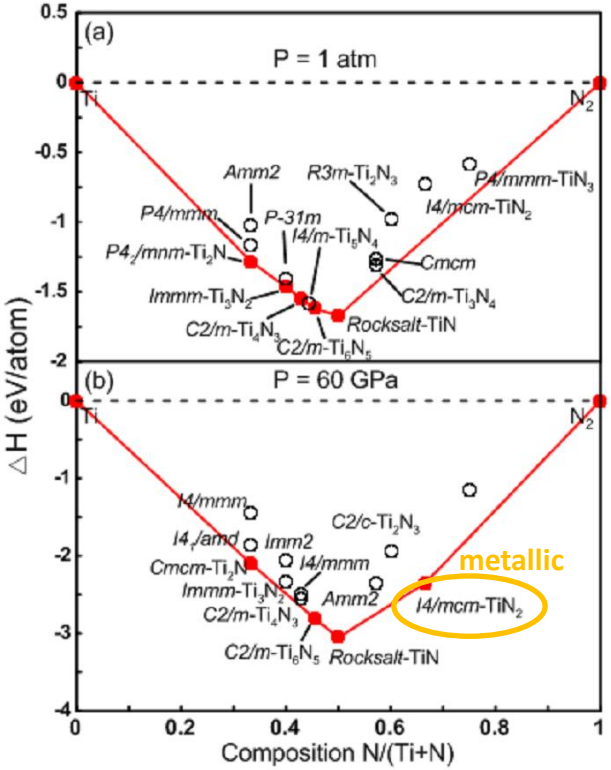
	Structure type	Space group
TiN_2	CaC_2-I	$I4/mmm$ (139)
	TiN_2-I	$Pmn2_1$ (31)
	CaC_2-V	$Immm$ (71)
	ThC_2	$C2/c$ (15)

Bandgap= 0.8 eV

Kulkarni et. al, chem. Asian J. 8, 743 (2013)

Experiments on the synthesis of titanium nitride were performed at pressures between 17.5 and 25 GPa, and temperatures between 1,500 K and 3,000 K. In the experiments with titanium metal as a starting material, we observed formation of δ-TiN with NaCl structure and a metastable ω-phase of the residual titanium. The ω-phase appeared on compression of the starting α-Ti above about 2 GPa and remains after pressure release[29,30]. In experiments with δ-TiN as a starting material, no changes were found at high pressures and after recovery. Thus, we have

Zerr et al, Nat. Mater.,2, 185 (2003)



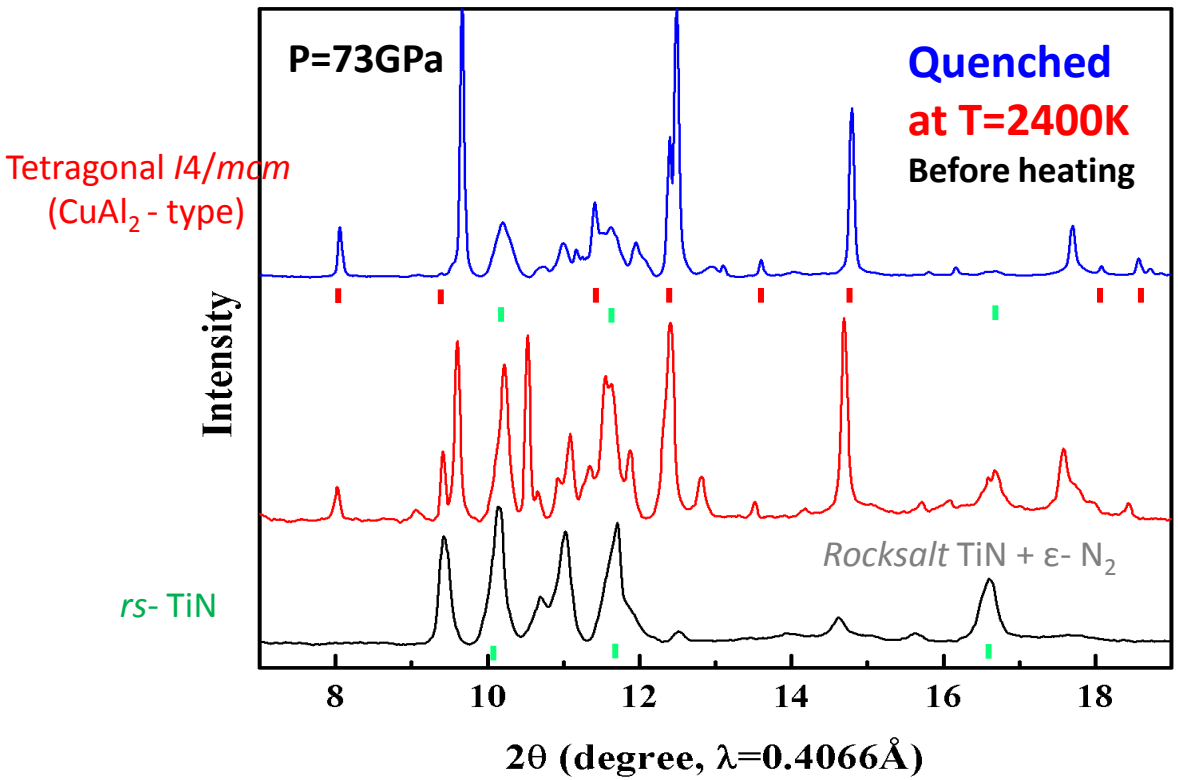
Shuyin Yu et. al, PCCP, 17, 11763 (2015)

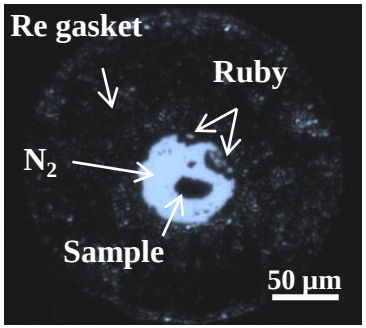
Starting material: TiN + N_2

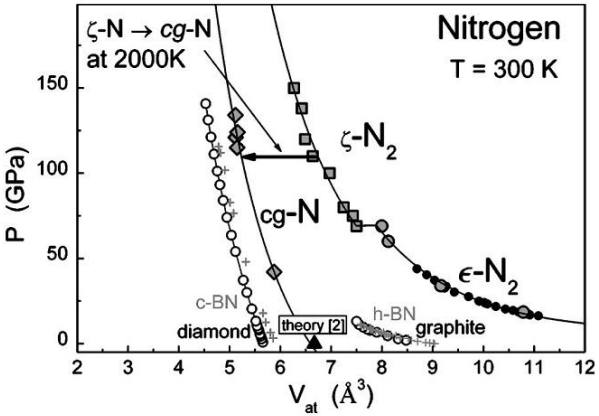
Pressure: > 60 GPa

Synthesis of TiN_2

$$TiN + \tfrac{1}{2} N_2 \xrightarrow[\sim 2400K]{73GPa} TiN_2 \; ???$$



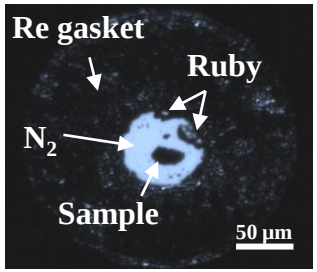




M. Eremets et al, J. Chem. Phys. 121, 11296 (2004)

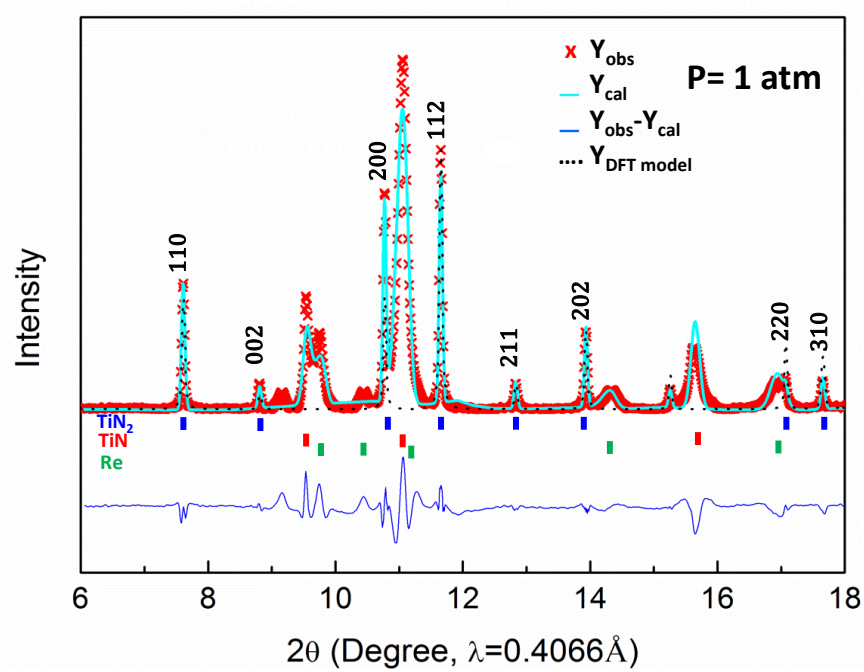
High Pressure Collaborative Access Team

Synthesis of TiN_2



Laser Heated Diamond Anvil Cell

$$TiN + \frac{1}{2} N_2 \xrightarrow[\sim 2400K]{73GPa} TiN_2 \; ???$$



Tetragonal *I4/mcm*
***a*=*b*=4.334(1)Å**
***c* =5.294(2)Å**

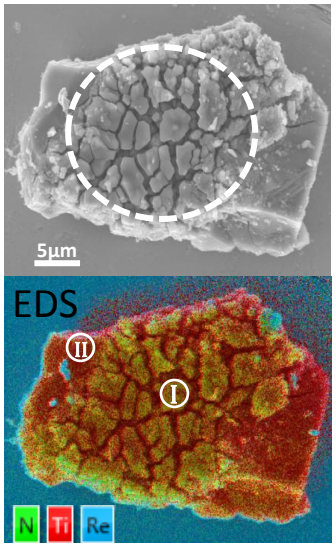
***N @8h* (*x* = 0.1124)**

Shuyin Yu et al, PCCP, 17, 11763 (2015)

Stoichiometry in the heated region

$TiN_2 - TiN_{2.25}$

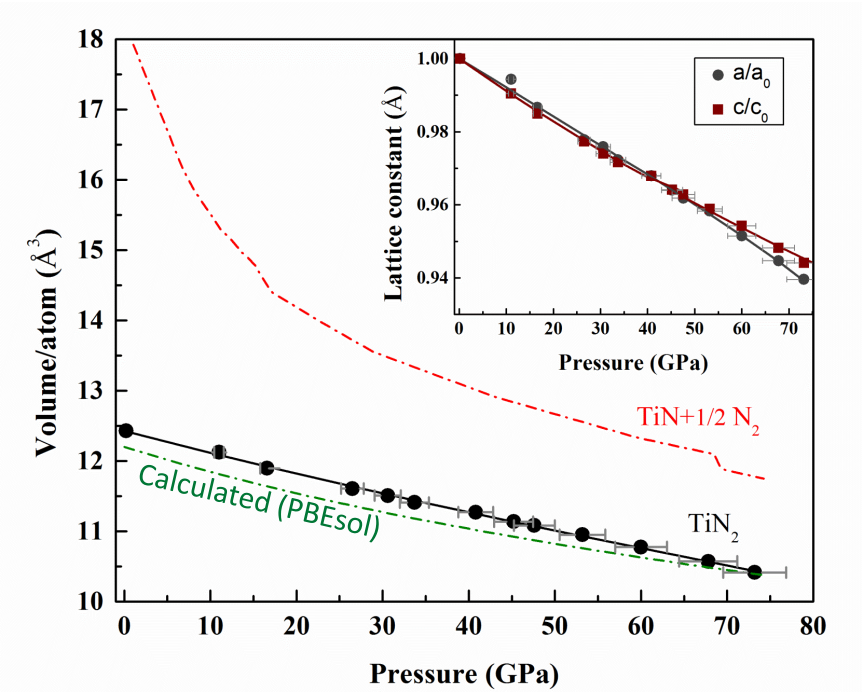
Topography related errors in EDS



At%	I	II
Ti	28.2±0.4	49.0±0.9
N	64.8±0.6	48.9±1.6

The new compound is tetragonal TiN_2

EOS of TiN_2



Method	V(Å^3)	K_0(GPa)	K_0'
LDA	95.08	347	3.3
PBE	98.44	293	3.7
PBEsol	97.61	328	4.0
Expt.	99.44	**385(7)**	1.45(18)

K_0 of *c*-BN = 382 GPa

TiN_2 is ultraincompressible!!

3rd order B-M EOS

$$P(V) = \frac{3K_0}{2}\left[\left(\frac{V_0}{V}\right)^{\frac{7}{3}} - \left(\frac{V_0}{V}\right)^{\frac{5}{3}}\right]\left\{1 + \frac{3}{4}(K_0' - 4)\left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right]\right\}$$

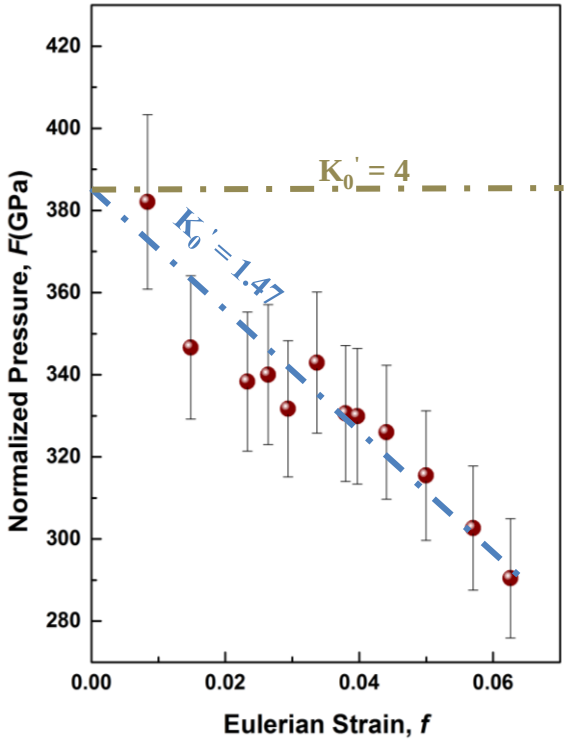
K_0' value is too low!!

Poor choice of EOS or deviatoric stress??

2nd order truncation ($K_0' = 4$) ⟹ K_0 = 318 (11) GPa

EOS of TiN_2

2nd order vs 3rd order EOS



R. J. Angel, *High Temperature High Pressure Crystal Chemistry* (2000)

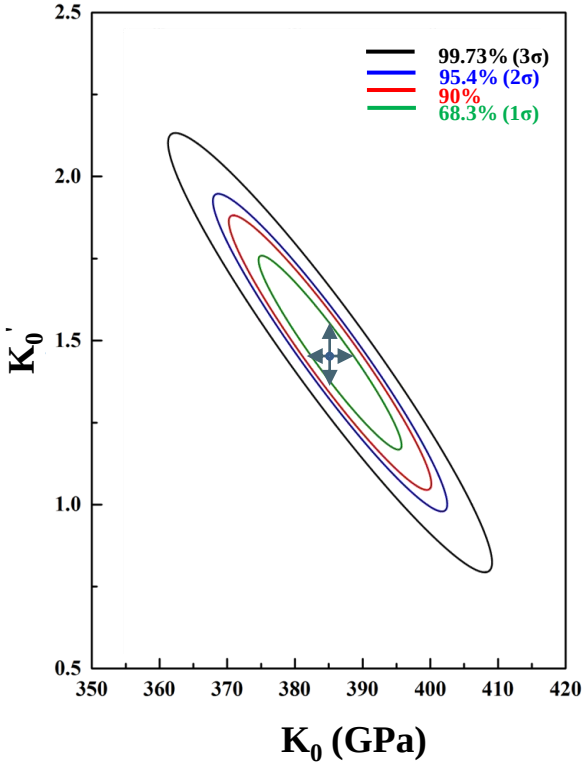
3rd order EOS is suitable

$$F = P \Big/ 3f(1+2f)^{5/2}$$

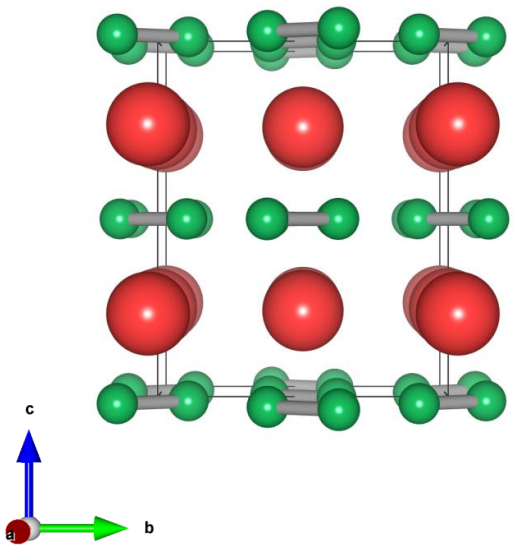
$$f = \frac{\left[\left(\frac{V_0}{V}\right)^{2/3} - 1\right]}{2}$$

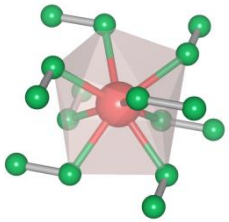
bulk modulus > 360 GPa

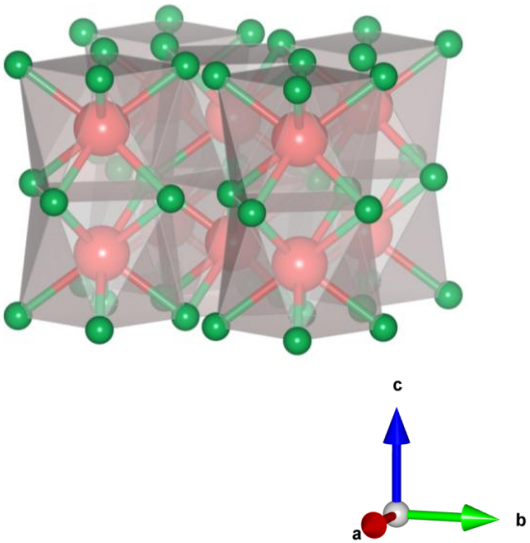
K_0, K_0' correlate heavily!!



Crystal Structure of TiN_2

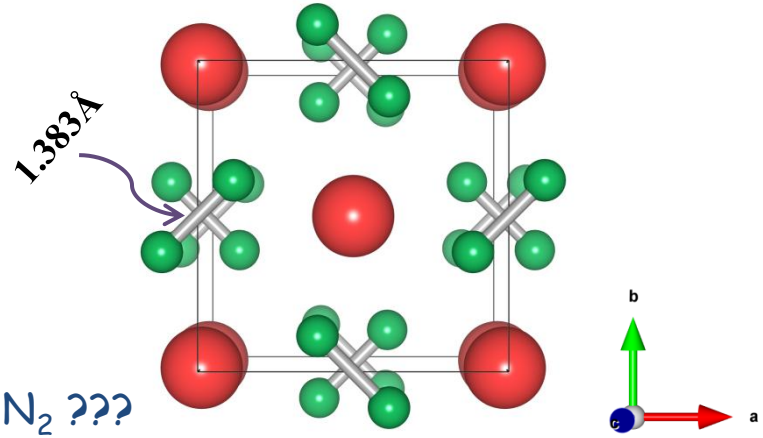






- ❑ $CuAl_2$ –type; Z= 4
- ❑ TiN_8 antiprisms
- ❑ N_2 dumbbels
- ❑ Ti, N_2 layers along c-axis

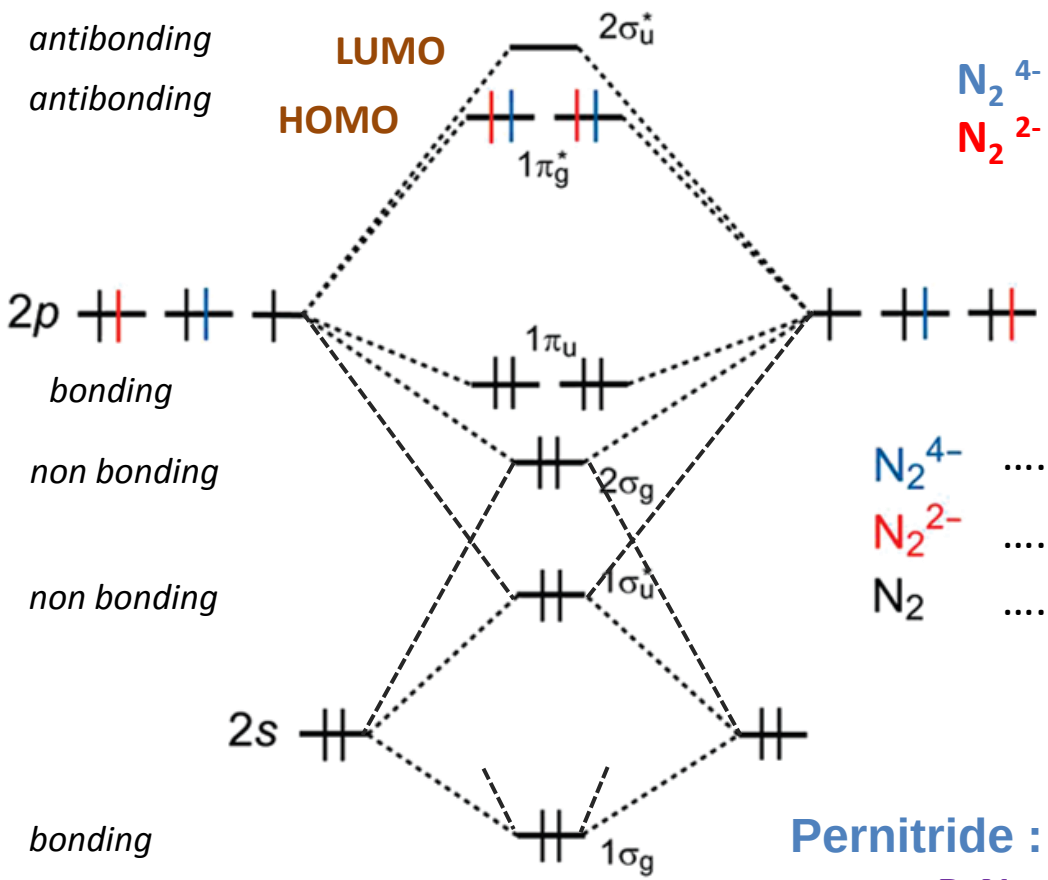
- ❑ Dihedral angle b/n two N_2 dumbbells
  along a-axis: 180^0
  c-axis: 86.3^0
- ❑ N_2 dumbbells orient to minimize steric hindrance
- ❑ N-N bondlength is comparable to F-F (1.42Å)



What is the bond order of nitrogen in TiN_2 ???

TiN_2 – pernitride (Ti^{4+} $(N_2)^{4-}$) or diazanide (Ti^{2+} $(N_2)^{2-}$) ???

Pernitride vs Diazanide



N_2^{4-} = Pernitride ion (Bond order=1)

N_2^{2-} = Diazanide ion (Bond order=2)

N_2^{4-} ..... Isoelectronic to F−F (l =1.42Å)

N_2^{2-} ..... Isoelectronic to O = O (l =1.21Å)

N_2 ..... N≡N (l =1.10Å)

Pernitride :

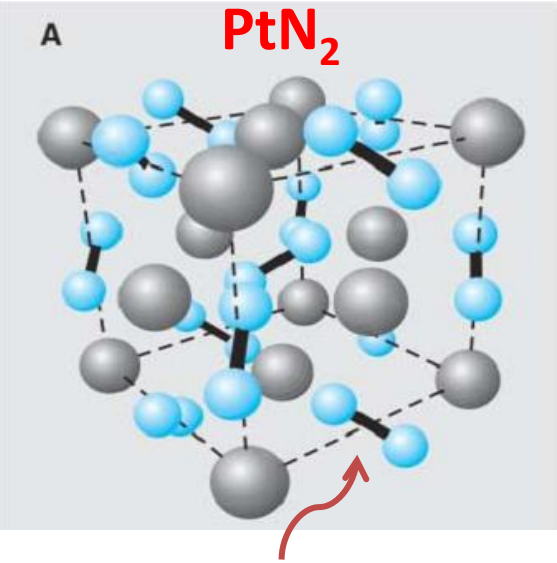
PtN_2, IrN_2, OsN_2, PdN_2 , RuN_2 and RhN_2

Diazanide :

BaN_2, CaN_2, SrN_2

M. Wessel et al, J. Am. Chem. Soc., 132, 2421 (2010)

Pernitride vs Diazanide



Single N−N bond length: 1.41 Å

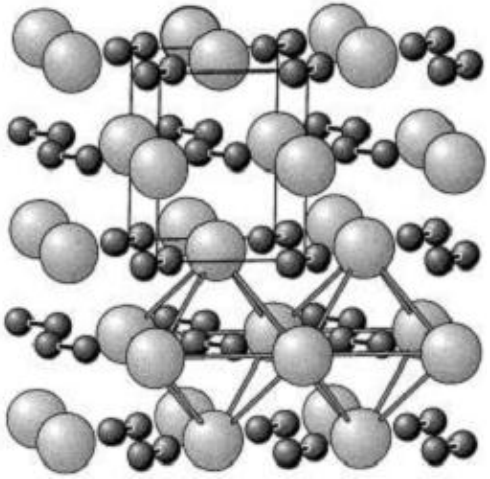
J. C. Crowhurst et al, Science, 311, 1275 (2006)

Pyrite structure (space group: *Pa*-3*m*)

Bulk modulus = 350-410 GPa

Semiconductor with E_g = 1.5 eV (Indirect)

BaN_2



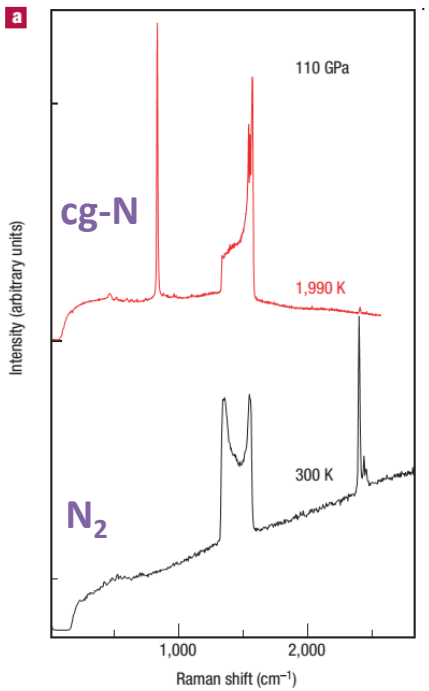
Tetragonal *I*4/*mmm*

Bulk modulus = 46 GPa

metallic

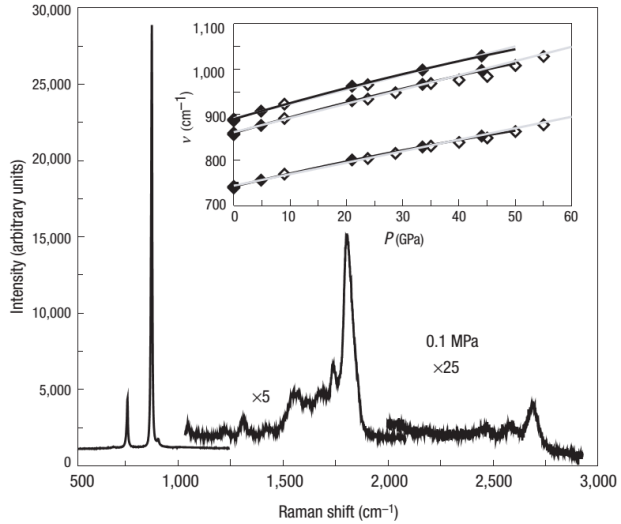
G. V. Vajenine et al, Inorg. Chem., 40, 4866 (2001)

Raman modes of TiN_2



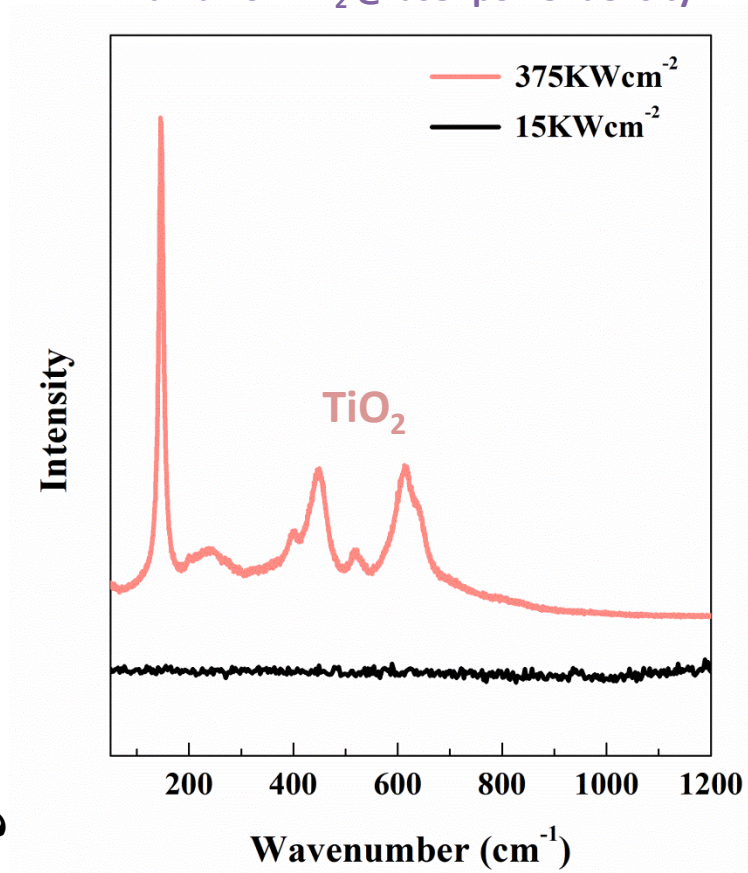
M. Eremets et al, Nat. Mater., 3, 558 (2004)

PtN_2



E. Gregoryanz et al, Nat. Mater., 3, 294 (2004)

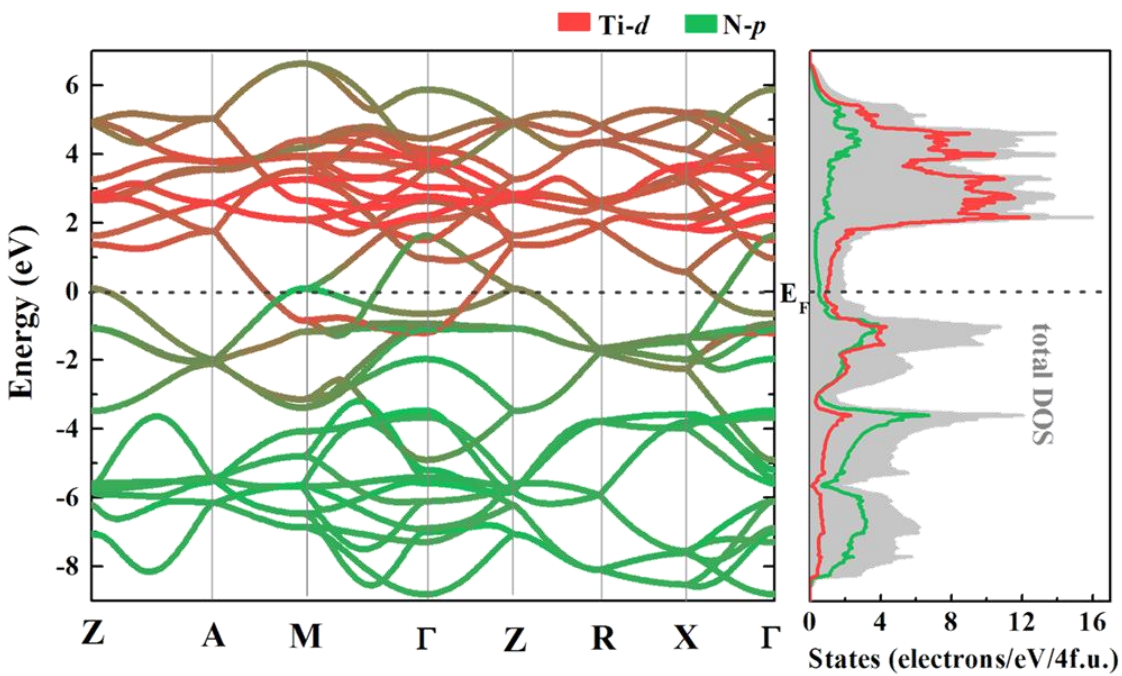
Raman of TiN_2 @laser power density



Is TiN_2 a metal ???

TiN_2 is thermally unstable!!

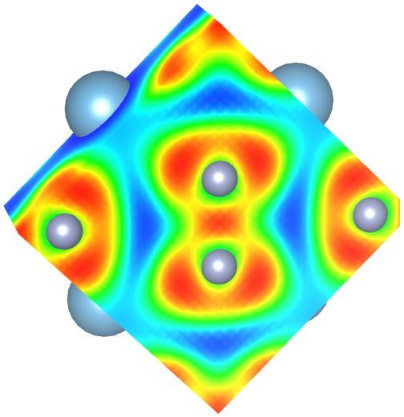
Electronic band structure



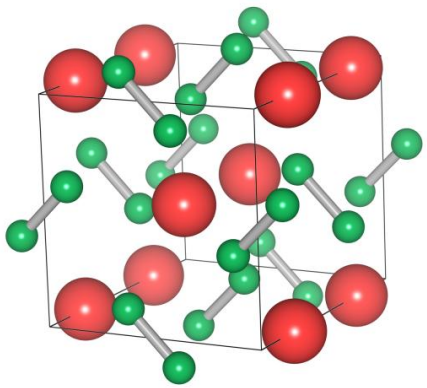
- DFT calculations using PBEsol
- TiN_2 is metallic
- metallicity originates from Ti-d, Ti-d/N-p hybrid electrons
- Pseudo gap between occupied and unoccupied states indicate covalency

Bonding Character

ELF > 8



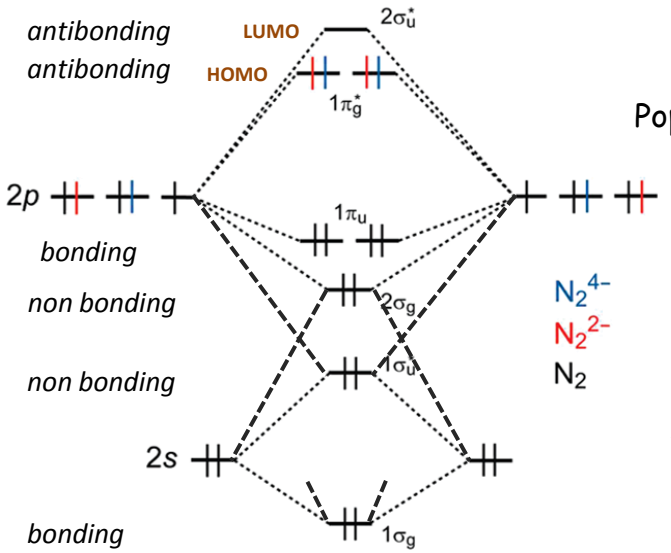
Large ELF between 'N' atoms
- covalent N-N bond



TiN_2 = Titanium Pernitride

N–N stretching mode				N–N bond length
PtN_2				
ν_s = 850 cm^{-1}	→	Single bond	←	l = 1.42 Å
TiN_2				
ν_s (cal) ~ 1150 cm^{-1}	→	~Single bond	←	l = 1.38 Å (cal)
BaN_2				
ν_s = 1466 cm^{-1}	→	Double bond	←	l = 1.23 Å

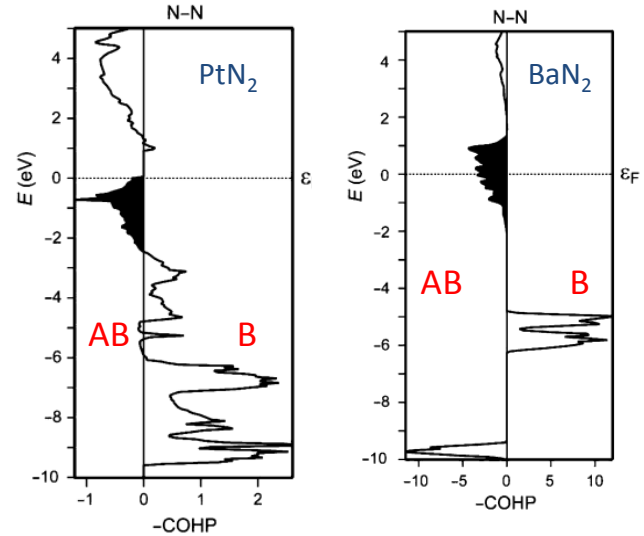
Origin for incompressible nature



Populated $1\pi_g$ * anti-bonding orbitals

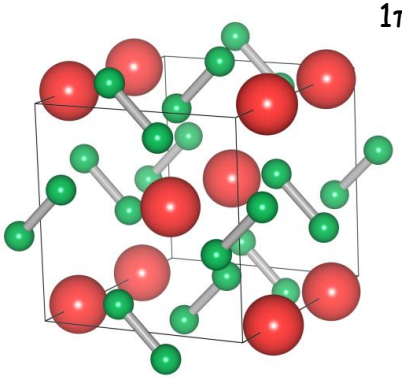
repulsion between N atoms

Incompressibility of the whole system



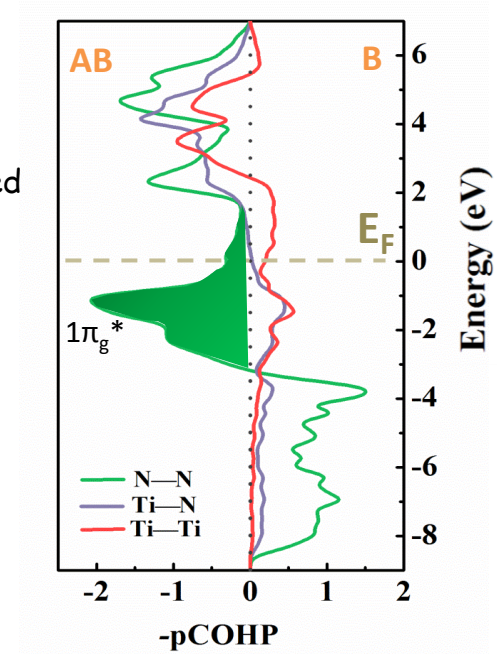
COHP= Crystal Orbital Hamilton Population
"Bond-weighed DOS"

M. wessel et al, J. Am. Chem. Soc., 132, 2421 (2010)

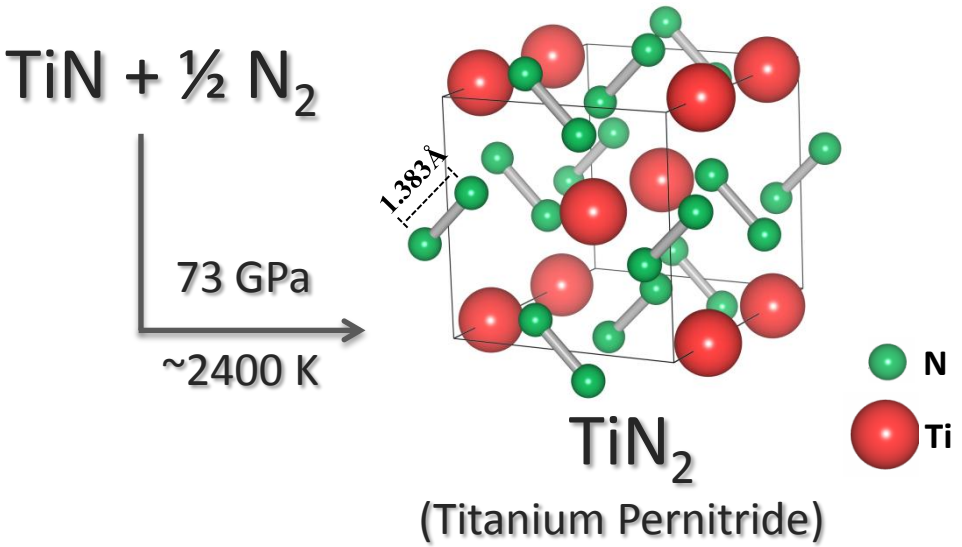


$1\pi_g$ * anti-bonding orbitals are almost completely filled

Incompressible TiN_2 – Titanium Pernitride



Conclusions



- ✓First non-noble metal pernitride
- ✓ Ultraincompressible metal
- ✓ Bulk modulus >360 GPa

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Acknowledgements

- Dr. John Armstrong for helping us with EDS measurements
- Dr. Ross Hrubiak, Dr. Huiyang Gou for helping us with XRD measurements at HPCAT

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Thank You