

## **Semiconductors with Chiral Crystal Structure in Group**

### **IVB Transition Metal Pernitrides**

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Table S1. The bond lengths ( $\text{\AA}$ ) of N-N ( $d_{\text{N-N}}$ ) and TM-N bond, volume ( $\text{\AA}^3$ ) and band gap (eV) calculated by PBE and HSE06 at ambient pressure for  $P3_121$ -TMN<sub>2</sub>.  $d1-d4$  denote four type TM-N bonds marked in Figure 1 (c).

	$d_{\text{N-N}}$	$d1$	$d2$	$d3$	$d4$	volume	Band Gap	
							PBE	HSE06
TiN <sub>2</sub>	1.385	2.076	2.145	2.275	2.403	76.42	0.413	1.076
ZrN <sub>2</sub>	1.440	2.229	2.308	2.418	2.524	91.86	0.703	1.341
HfN <sub>2</sub>	1.467	2.199	2.273	2.385	2.504	89.27	1.089	1.838

Table S2. Calculated lattice constants and Wyckoff Position for TiN<sub>2</sub> at 0 GPa.

Phase	lattice constants ( $\text{\AA}$ )	Wyckoff Position				
		atom	position	x	y	z
$P3_121$	$a=b=4.147, c=5.130$ $\alpha=\beta=90^\circ, \gamma=120^\circ$	Ti	3a	0.0000	0.6450	0.6667
		N	6c	0.1602	0.8002	0.0915
$P3_221$	$a=b=4.147, c=5.130$ $\alpha=\beta=90^\circ, \gamma=120^\circ$	Ti	3a	0.6451	0.0000	0.6667
		N	6c	0.3601	0.2000	0.4249

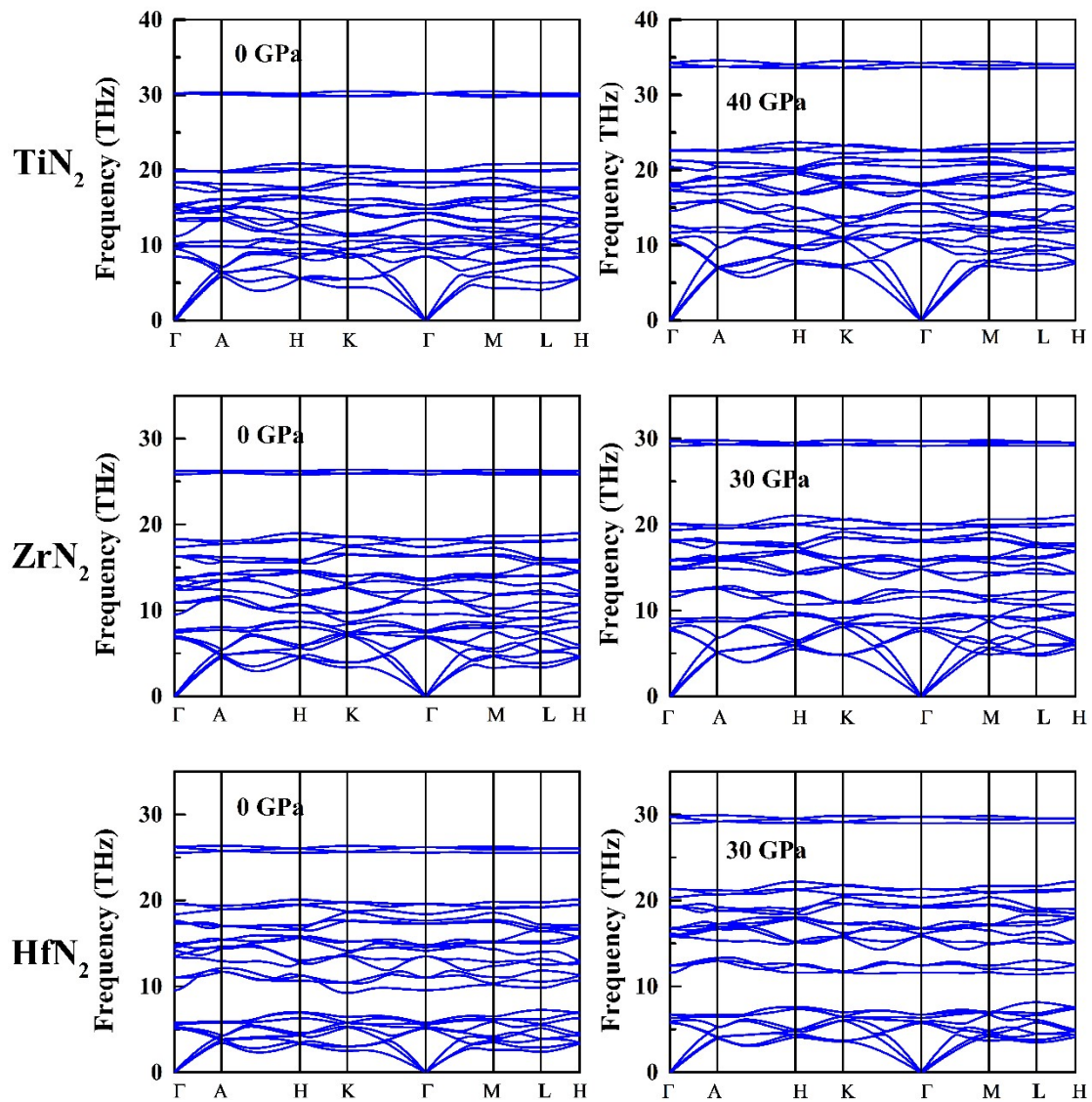


Figure S1. Phonon spectrum of  $P3_121$ - $\text{TMN}_2$  at 0 GPa and high pressure.

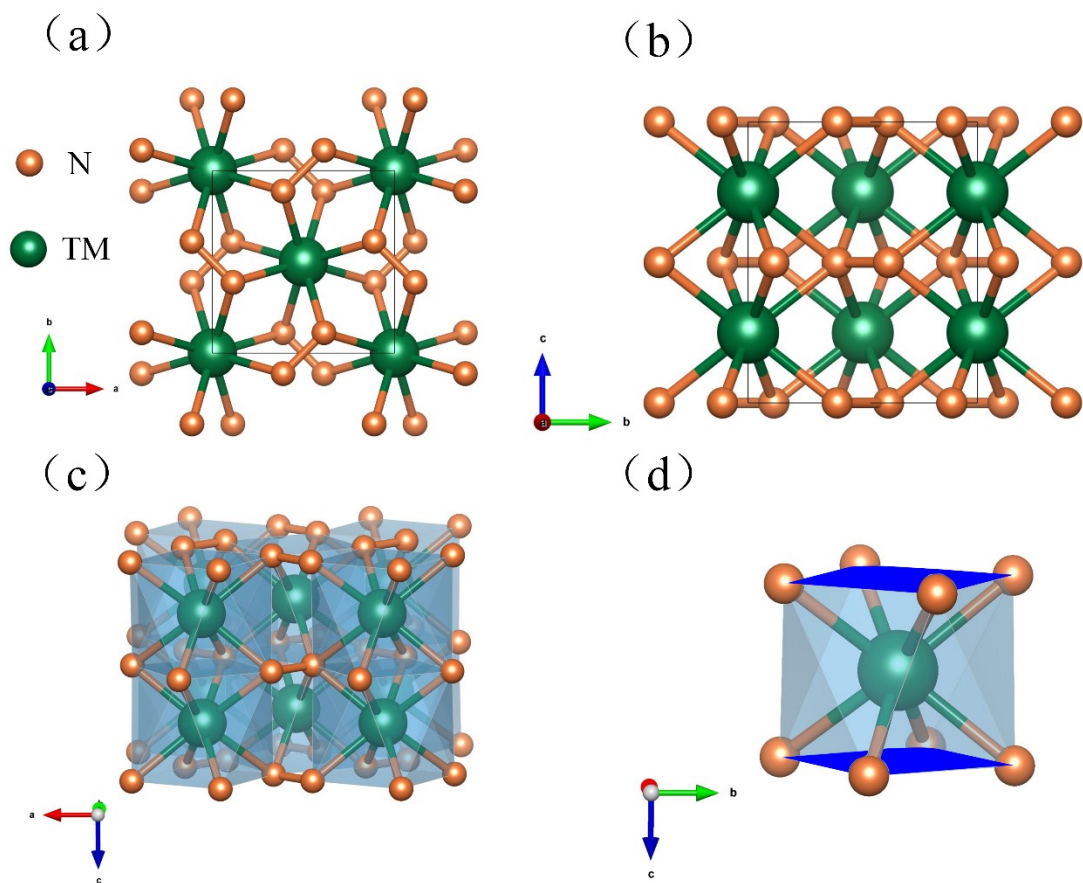


Figure S2. Crystal structure of  $I4/mcm$ - $\text{TMN}_2$  for view of (a)  $[001]$  and (b)  $[100]$  direction. (c) conventional unit cell with decanedrons and (d) diagram of a single decanedron. The blue planes denote the N atom layers. The up plane of decanedron is parallel to the bottom plane, and the rotation angle from up N layer to bottom N layer are  $32.23^\circ$  (anticlockwise) or  $57.77^\circ$  (clockwise).

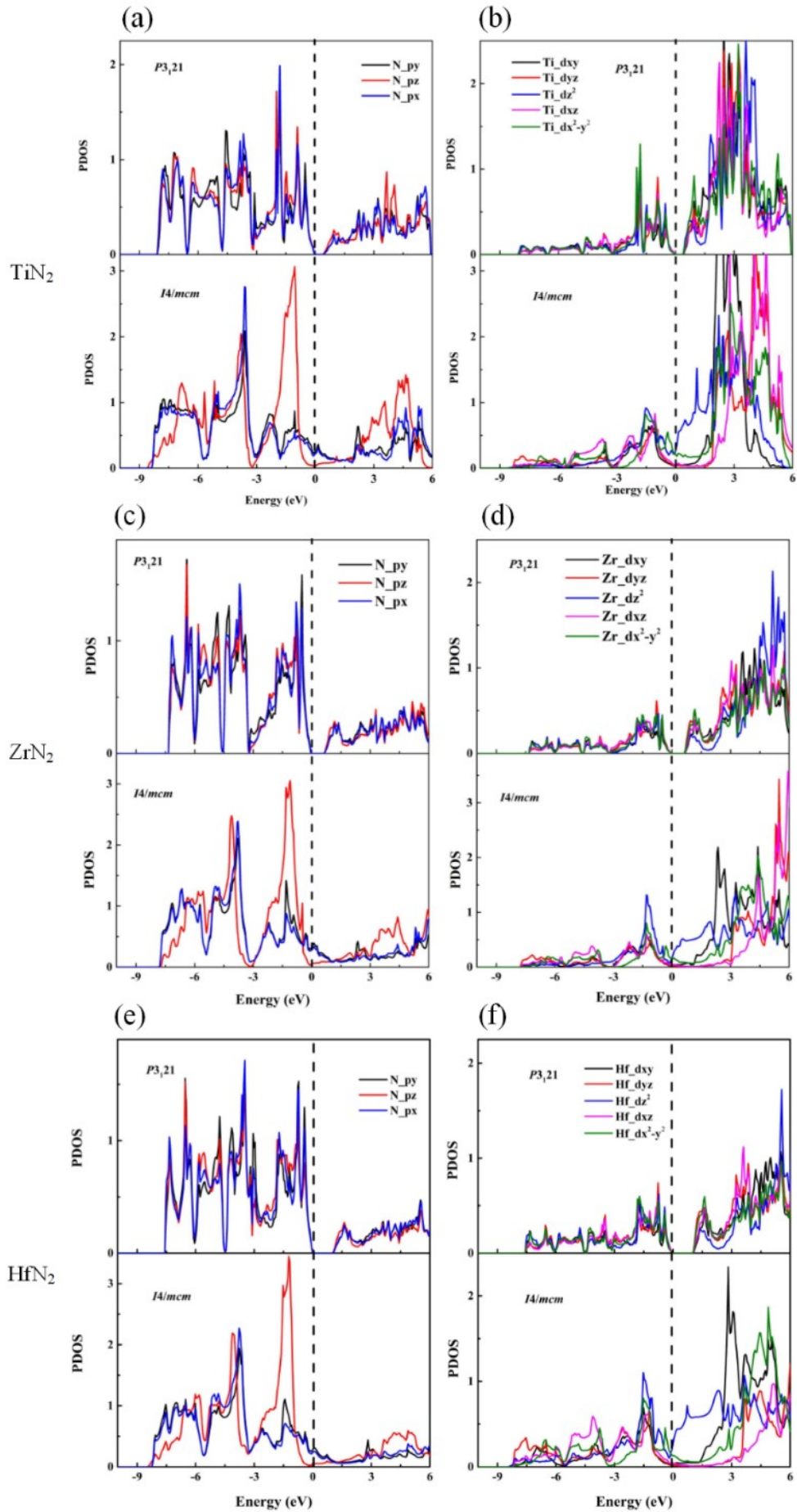


Figure S3. Projected density of state (PDOS) of N<sub>2</sub>p and TM<sub>d</sub> orbitals of *P3<sub>1</sub>21* (up panel) and *I4/mcm* (bottom panel) phases for (a) and (b) TiN<sub>2</sub>, (c) and (d) ZrN<sub>2</sub>, and (e) and (f) HfN<sub>2</sub>, respectively. The partial orbital of N<sub>p</sub> (N<sub>py</sub>, N<sub>pz</sub>, and N<sub>px</sub>) and TM<sub>d</sub> (TM<sub>dxy</sub>, TM<sub>dyz</sub>, TM<sub>dz<sup>2</sup></sub>, TM<sub>dxz</sub>, and dx<sup>2</sup>-y<sup>2</sup>) of *P3<sub>1</sub>21* phase show nearly evenly contribution in the -8-6 eV energy ranges, respectively. However, in *I4/mcm* phase, the orbital contribution of N<sub>pz</sub> are not the same as that of N<sub>py</sub> and N<sub>px</sub>, and the projected orbital of TM<sub>d</sub> show different contribution, such as the mainly contribution of dz<sup>2</sup> for 0-2 eV. It is indicated that there is significant difference between *P3<sub>1</sub>21* and *I4/mcm* structures on the contribution of partial orbitals of N<sub>2</sub>p and TM<sub>d</sub> orbitals.

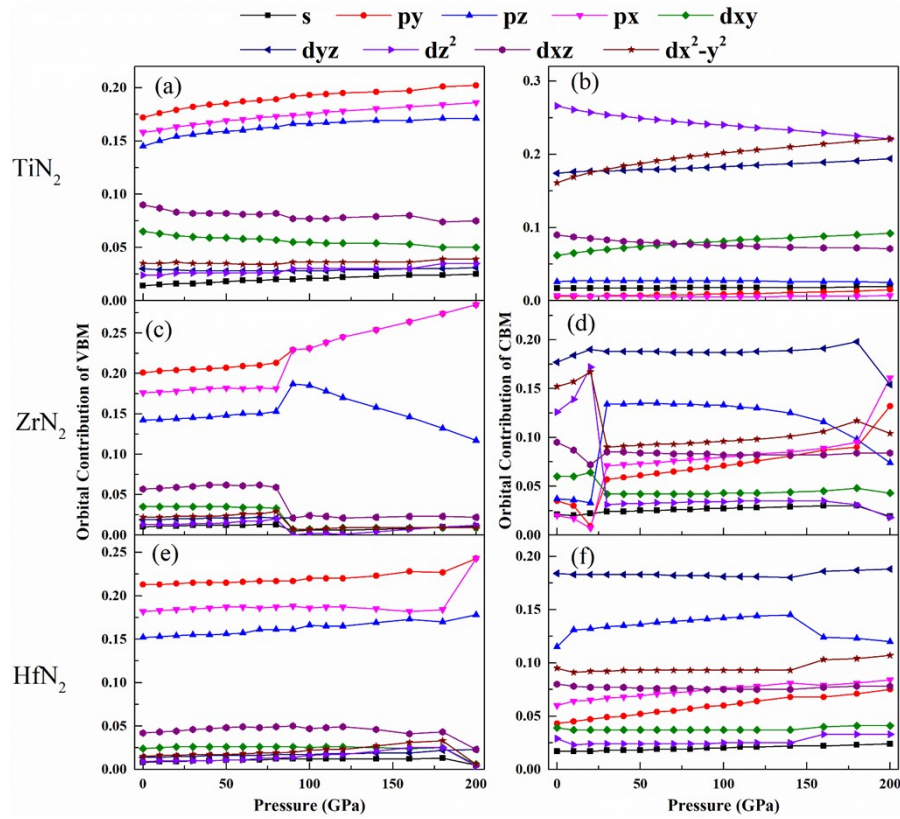


Figure S4. Projected orbital contribution of VBM and CBM as a function of pressure in *P3<sub>1</sub>21* phase.

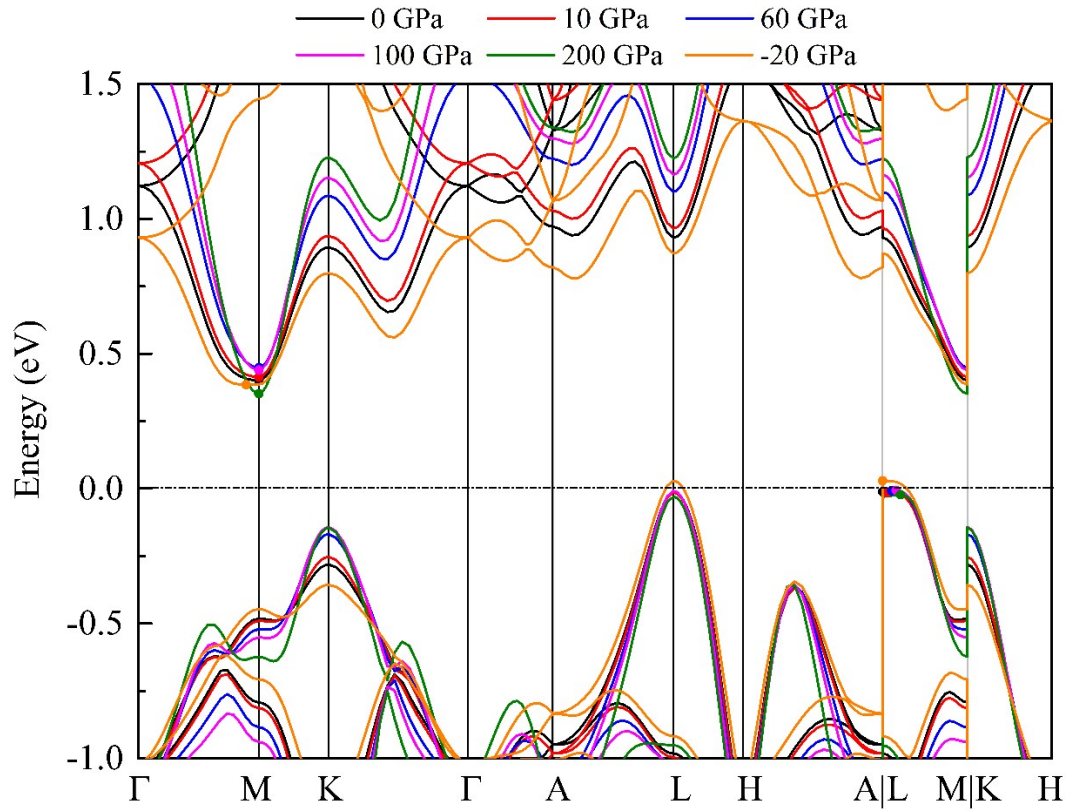


Figure S5. Band structure of  $P3_121$ - $\text{TiN}_2$  at ambient and high pressure. The CBM is at M point in the pressure range 0-200 GPa, while the CBM is on the line between  $\Gamma$  and M at -20 GPa (the negative sign represents the applied hydrostatic expansion pressure). The VBM at 0 and -20 GPa is at L point, and with the pressure of increase, the VBM moves from L point to the point between L and M.

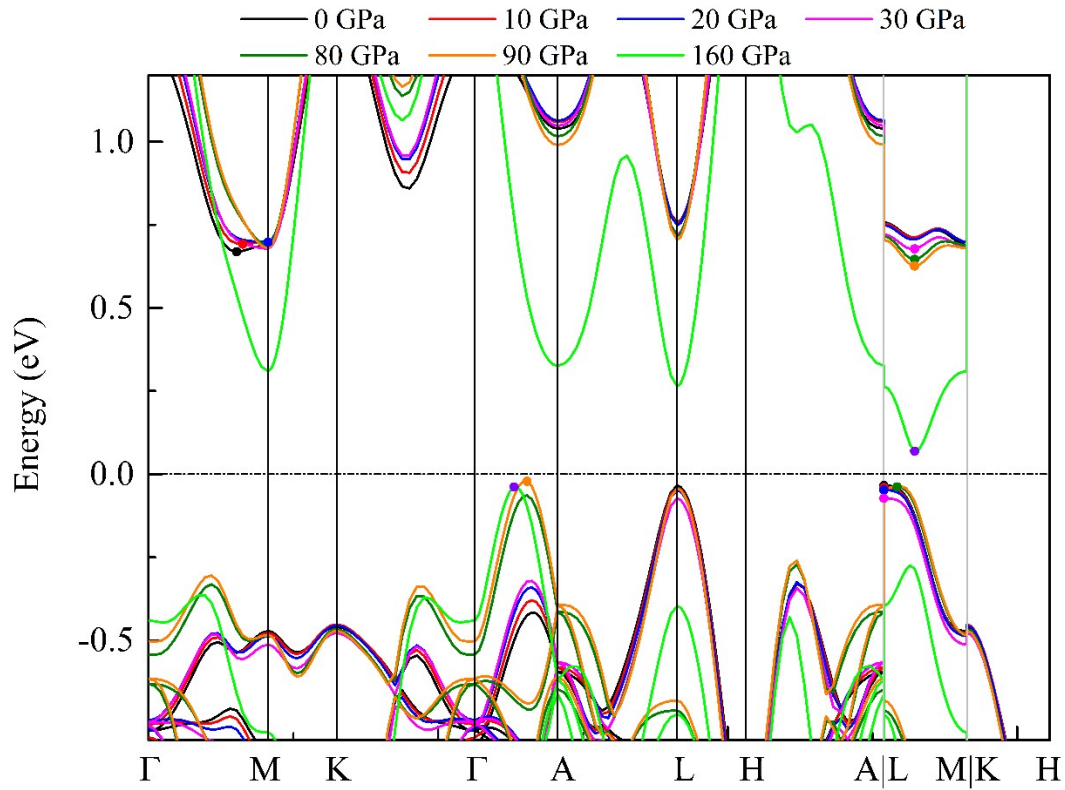


Figure S6. Band structure of  $P3_121\text{-ZrN}_2$  at ambient and high pressure. The VBM in the 0-40 GPa pressure range is at L point, and with the pressure of increase (40-80 GPa), the VBM moves from L point to the point between L and M, and then in the pressure range of 90-200 GPa, the VBM is on the line between  $\Gamma$  and A point. The CBM is between  $\Gamma$  and M point at 0-10 GPa, and at 20 GPa the CBM is at M point, but with increasing of pressure (30-200 GPa), the CBM is between L and M point.



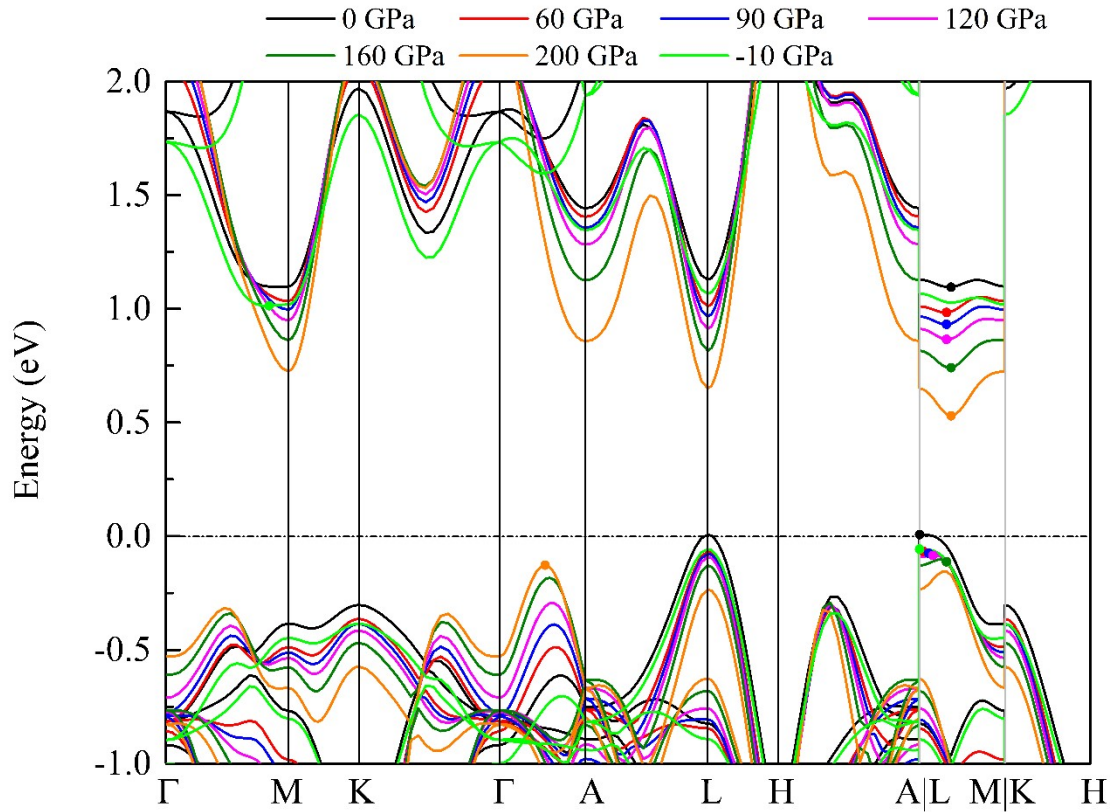


Figure S7. Band structure of  $P3_121\text{-HfN}_2$  at ambient and high pressure. The CBM is located on the line between L and M point in the pressure range of 0-200 GPa, but is located on the line between  $\Gamma$  and M point at -10 GPa (the negative sign represents the applied hydrostatic expansion pressure). It should be noted that the CBM at 0 and 160-200 GPa is on the same k-point, while the CBM at 10-140 GPa is located on the other one k-point. In the pressure range of -10-50 GPa, the VBM is at L point. With the pressure of increasing (50-180 GPa), the VBM moves from L point to the point between L and M, and then moves the point between  $\Gamma$  and A at the pressure of 200 GPa.

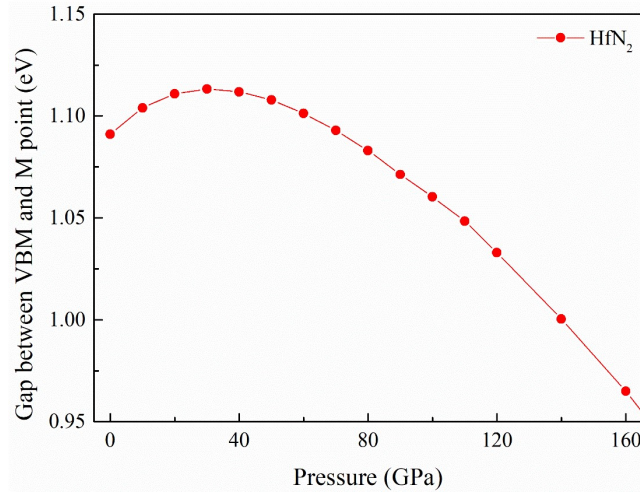


Figure S8. The energy gap between VBM and M point of conduction band for  $P3_121$ -HfN<sub>2</sub>.

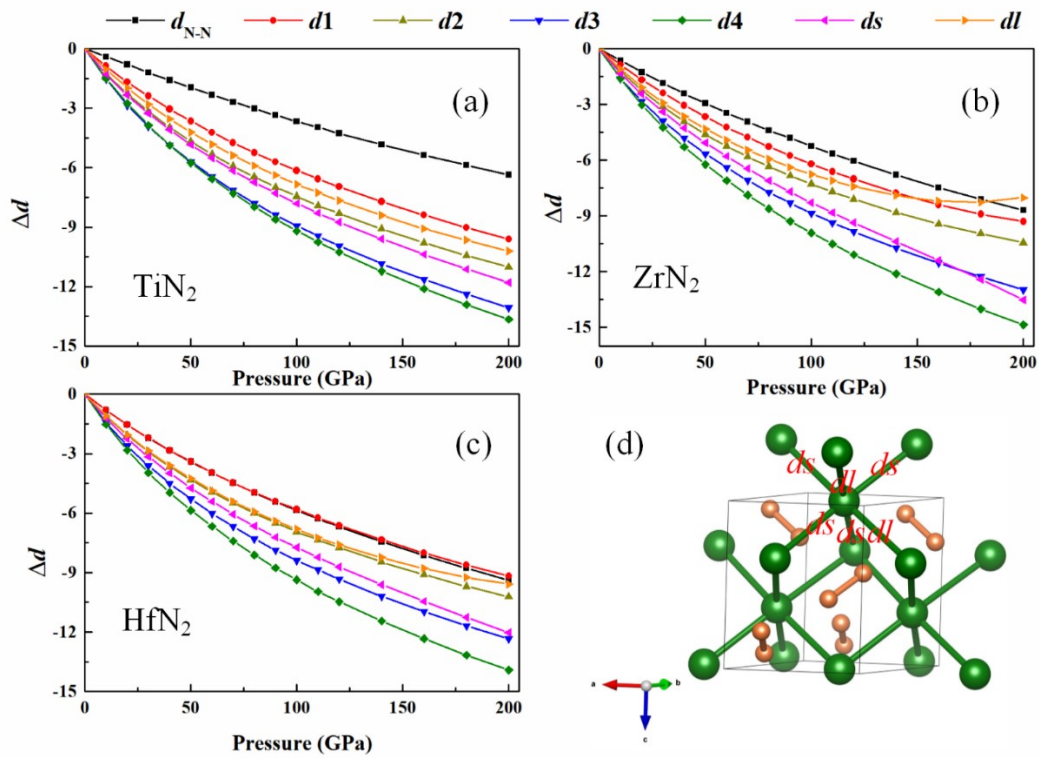


Figure S9. The variation of bond lengths of N-N, TM-N, and TM-TM bond of  $P3_121$  structure

expressed in percent ( $\Delta d = \frac{d - d_0}{d_0} * 100\%$ , where  $d_0$  and  $d$  are the bond lengths at zero and high pressure, respectively.) as a function of pressure for (a) TiN<sub>2</sub>, (b) ZrN<sub>2</sub>, and (c) HfN<sub>2</sub>. (d) Crystal structure of  $P3_121$  with the TM-TM and N-N bonds, and the  $d_s$  and  $d_l$  are the shorter and longer bond length of TM-TM bonds, respectively.

Table S3. The calculated bulk modulus B, shear modulus G, and Vickers hardness  $H_v$  (in units of GPa) for c- $Zr_3N_4$  and c- $Hf_3N_4$  at ambient pressure.

	B		G		$H_v$	
	This works	Theory <sup>a</sup>	This works	Theory <sup>a</sup>	This works	Theory <sup>a</sup>
c- $Zr_3N_4$	225.8	218.3	127.1	129.3	14.4	15.6
c- $Hf_3N_4$	241.3	228.1	139.1	138.1	15.8	16.9

<sup>a</sup>Ref<sup>1</sup>

### Reference

1. Mattesini, M.; Ahuja, R.; Johansson, B., Cubic  $Hf_3N_4$  and  $Zr_3N_4$ : A class of hard materials. *Physical Review B* **2003**, *68* (18).