# Supplementary Information
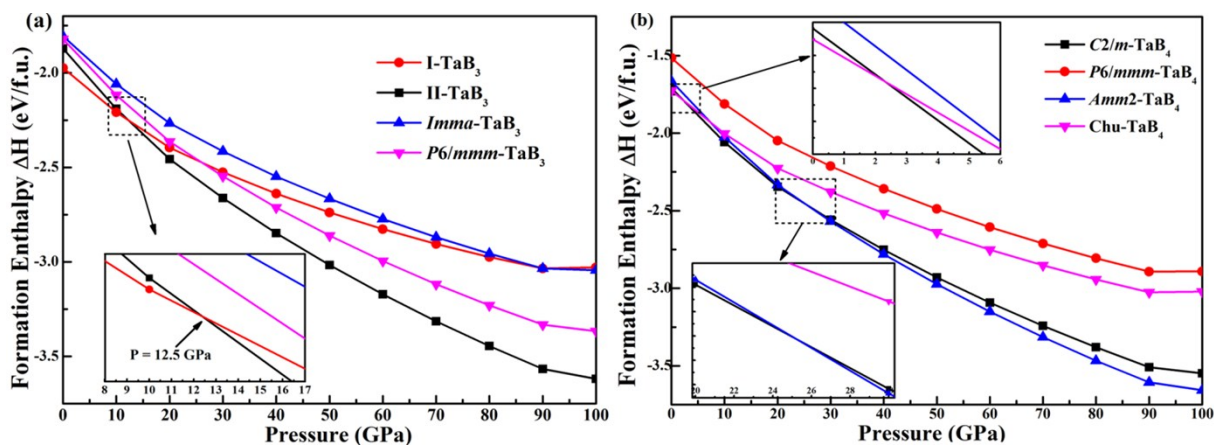


**Fig. S1** The formation enthalpies of (a) $TaB_3$ and (b) $TaB_4$ relative to (Ta + B).
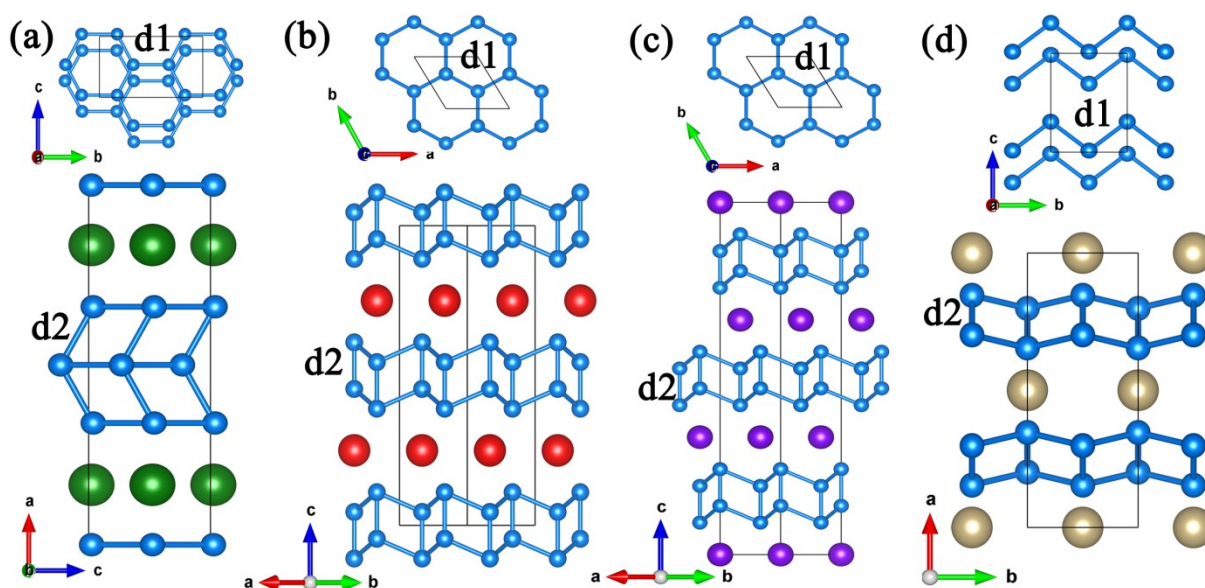


**Fig. S2** Crystal structures for (a) $Amm2$-$TaB_4$, (b) $WB_4$, (c) $ReB_4$, and (d) $OsB_4$.
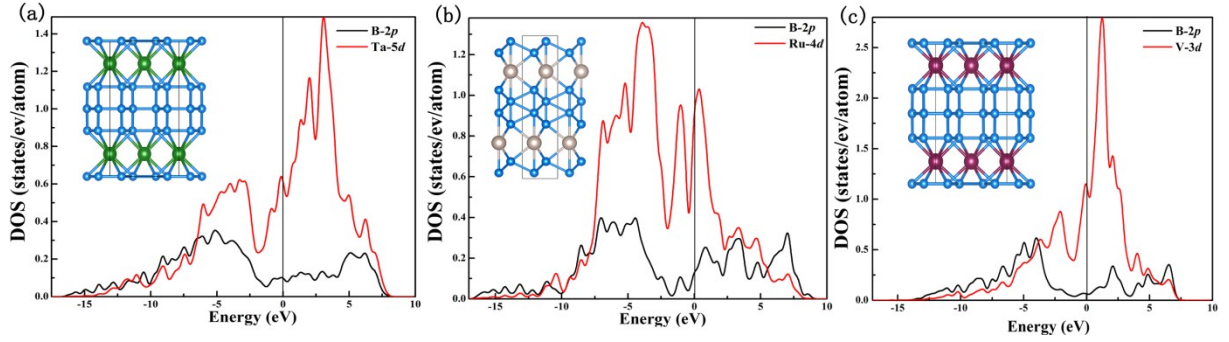
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**Fig. S3** Partial density of states (PDOS) of two nearest-neighbour B atom and TM (TM = Ta, Ru, and V) atom for (a) *Amm*2-TaB$_4$, (b) $P6_3/mmc$-RuB$_4$ and (c) *Amm*2-VB$_4$. Their crystal structures are shown in the inset.
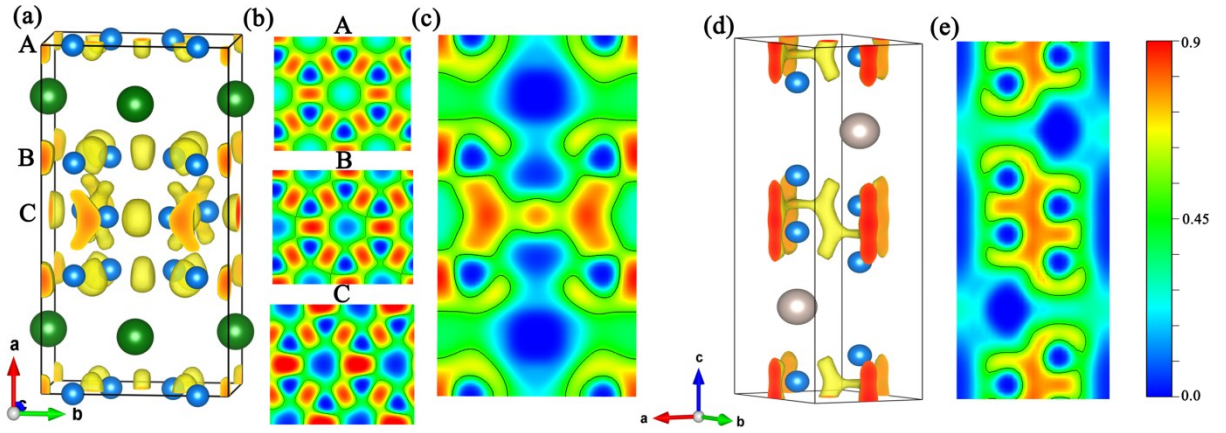


**Fig. S4** Contours of ELF = 0.75 for *Amm*2-TaB$_4$ (a), three (100) planes for *Amm*2-TaB$_4$ (b), (001) for *Amm*2-TaB$_4$ (c), contours of ELF = 0.75 for $P6_3/mmc$-RuB$_4$ (d), and (110) plane of $P6_3/mmc$-RuB$_4$ (e).

**Table S1** Optimized equilibrium lattice parameters (Å and º), elastic constants ($C_{11}$, $C_{22}$, $C_{33}$) (GPa), bulk modulus $B$ (GPa), shear modulus $G$ (GPa), Young's modulus $Y$ (GPa), Poisson's ratio $\upsilon$, $B/G$ ratio.

| *Str.* | | *a* | *b* | *c* | $\gamma$ | $C_{11}$ | $C_{22}$ | $C_{33}$ | *B* | *G* | *Y* | $\upsilon$ | *B/G* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ***Amm*2-TaB$_4$** | This work | 9.961 | 5.285 | 3.111 | | 546 | 615 | 642 | 295 | 219 | 526 | 0.20 | 1.35 |
| $P6_3/mmc$-**WB$_4$** | Ref1 | 2.858 | 2.858 | 10.806 | 120 | 670 | | 1174 | 380 | 263 | 640 | 0.22 | 1.44 |
| $R$-$3m$-**ReB$_4$** | Ref2 | 2.938 | 2.938 | 16.325 | 120 | 563 | | 943 | 306 | 221 | 535 | 0.20 | 1.38 |
| $Pmmn$-**OsB$_4$** | Ref3 | 7.122 | 2.894 | 4.018 | | 580 | 590 | 608 | 285 | 217 | 519 | 0.20 | 1.31 |
| ***Amm*2-VB$_4$** | Ref4 | 9.292 | 5.187 | 3.062 | | 625 | 657 | 544 | 264 | 222 | 520 | 0.17 | 1.19 |
| $P6_3/mmc$-**RuB$_4$** | Ref5 | 2.943 | 2.943 | 10.590 | 120 | 442 | | 830 | 281 | 175 | 435 | 0.24 | 1.61 |

1.  Q. Li, D. Zhou, W. T. Zheng, Y. M. Ma, C. F. Chen, *Phys. Rev. Lett.* 2013, **110**, 136403.

2.  B. Wang, D.Y. Wang, Y.X. Wang, *J. Alloys Compd.*, 2013, **573**, 20-26.

3. M. Zhang, H. Yan, G. Zhang, H.J. Wang, *J. Phys. Chem. C*, 2012, **116**, 4293-4297.

4. L. Wu, B. Wan, Y. Zhao, Y. Zhang, H. Liu, Y. Wang, J. Zhang, H. Gou, *J. Phys. Chem. C*. 2015, **119**, 21649–21657.

5. Y. Wang, T. Yao, L.-M. Wang, J. Yao, H. Li, J. Zhang, H. Gou, *Dalton Trans.* 2013, **42**, 7041−7050.

# Born-Huang criterion:

For an orthorhombic crystal:

$C_{11} > 0, C_{22} > 0, C_{33} > 0, C_{44} > 0, C_{55} > 0, C_{66} > 0$,

$C_{11} + C_{22} + C_{33} + 2\left(C_{12} + C_{13} + C_{23}\right) > 0$,

$(C_{11} + C_{22} - 2C_{12}) > 0, (C_{11} + C_{33} - 2C_{13}) > 0,$

$(C_{22} + C_{33} - 2C_{23}) > 0,$

For a monoclinic crystal:

$C_{11} > 0, C_{22} > 0, C_{33} > 0, C_{44} > 0, C_{55} > 0, C_{66} > 0$,

$C_{11} + C_{22} + C_{33} + 2\left(C_{11} + C_{13} + C_{23}\right) > 0$,

$(C_{13}C_{55} - C_{35}^2) > 0, (C_{44}C_{66} - C_{46}^2) > 0, (C_{22} + C_{33} - 2C_{23}) > 0$

$[C_{22}(C_{33}C_{55} - C_{35}^2) + 2C_{23}C_{25}C_{35} - C_{23}^2C_{55} - C_{25}^2C_{33}] > 0,$

$g = C_{11}C_{22}C_{33} - C_{11}C_{23}^2 - C_{22}C_{13}^2 - C_{33}C_{12}^2 + 2C_{12}C_{13}C_{23},$

$\{2[C_{15}C_{25}(C_{33}C_{12} - C_{13}C_{23}) + C_{15}C_{35}(C_{22}C_{13} - C_{12}C_{23}) + C_{25}C_{35}(C_{11}C_{23} - C_{12}C_{13})] - [C_{15}^2($
$C_{22}C_{33} - C_{23}^2) +$

$C_{25}^2(C_{13}C_{33} - C_{13}^2) + C_{35}^2(C_{11}C_{22} - C_{12}^2)] + C_{55}g\} > 0$