Electronic Supplementary Material (ESI) for RSC Advances.


# Revealing the unusual rigid diamond net analogues in superhard tita nium carbides

Chunhong Xu[a], Kuo Bao*[a], Shuailing Ma[a], Da Li[a], Defang Duan[a], Hongyu Yu[a], Xilian Jin[a], Fubo Tian[a], Bingbing Liu[a], Tian Cui*[a]

*State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012, China*

**Figure S1**. The simulated power X-ray diffraction (λ= 0.5608 Å and the diffraction data are obtained from powder diffraction and not single crystal) for experiment structures (a) cubic TiC and (c) cubic $Ti_2C$ at ambient pressure, our predicted corresponding structures (b) TiC and (d) $Ti_2C$ at ambient pressure.

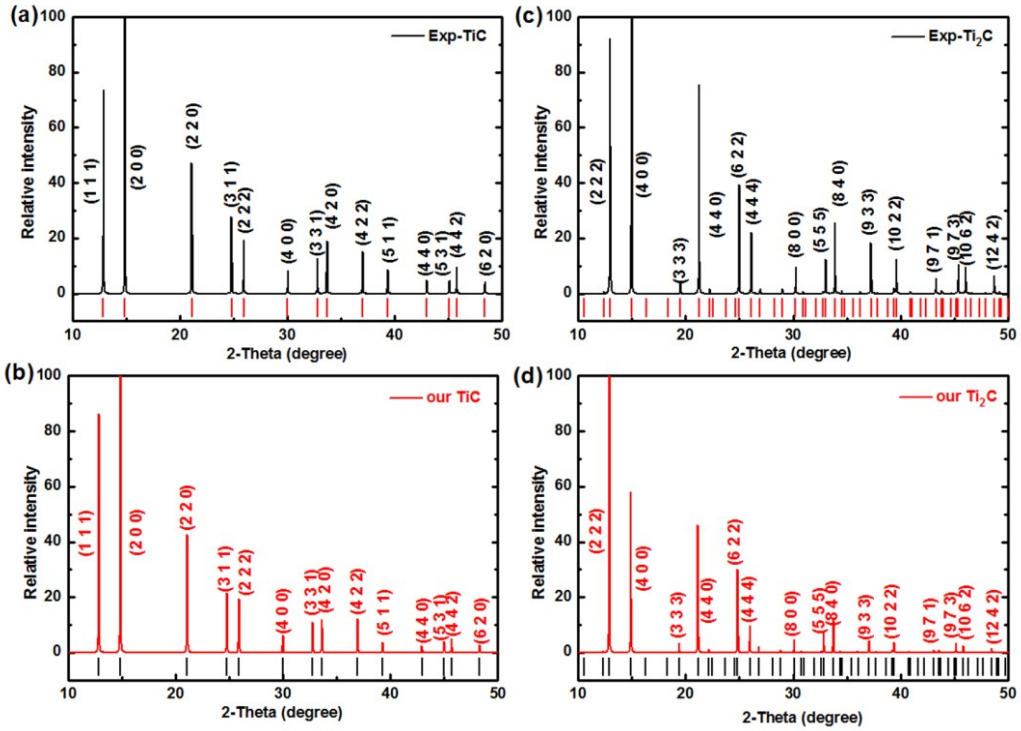

**Table S1**. Lattices parameters and atomic coordinates of $Ti_2C$, $Ti_3C_2$,$Ti_6C_5$, TiC-$TiC_4$ at ambient pressure.

| | Space Group | Lattice Parameters ( Å,° ) | Atoms | x | y | z |
|---|---|---|---|---|---|---|
| **$Ti_2C$** | *Fd*-3*m* | a=b=c=8.641 | Ti(32e) | -0.6312 | 0.1312 | 0.1312 |
| | | | C(16c) | -0.8750 | 0.3750 | 0.3750 |
| **$Ti_2C$** | *R*-3*m* | a=b=3.087,c=14.471 | Ti(6c) | 0.3333 | 0.6667 | 0.4212 |
| | | | C(3b) | 0.3333 | 0.6667 | 0.1667 |
| **$Ti_2C$** | *I*4/*m* | a=b=5.551,c=4.555 | Ti(8h) | 0.6604 | 0.8258 | 0.5 |
| | | | C(4e) | 0 | 0 | 0.3249 |
| **$Ti_2C$** | *I*4/*m* (Calc, Ref 1) | a=b=5.552,c=4.554 | Ti(8h) | 0.340 | 0.174 | 0 |
| | | | C(4e) | 0 | 0 | 0.825 |
| **$Ti_3C_2$** | *C*2/*m* | a=c=5.321,b=9.203 α=γ=90,β=70.197 | Ti(8j) | 0.2476 | 0.3400 | -0.2662 |
| | | | Ti(4i) | 0.2348 | 0.5 | -0.7428 |
| | | | C(2b) | 0 | 0.5 | 0 |
| | | | C(2c) | 0.5 | 0.5 | -0.5 |
| | | | C(4h) | 0 | 0.6676 | -0.5 |
| **$Ti_3C_2$** | *C*2/*m* (Calc, Ref 2) | a=c=5.219,b=9.038 α=γ=90,β=109.47 | Ti(8j) | 0.2531 | 0.1614 | 0.2373 |
| | | | Ti(4i) | 0.7379 | 0 | 0.2439 |
| | | | C(2a) | 0 | 0 | 0 |
| | | | C(4g) | 0 | 0.3327 | 0 |
| | | | C(2d) | 0 | 0.5 | 0.5 |
| **$Ti_3C_2$** | *P*4/*mbm* | a=b=5.315,c=2.855 α=γ=90,β=70.197 | Ti(2b) | 0 | 0 | 0.5 |
| | | | Ti(4g) | 0.1821 | 0.6821 | 0 |
| | | | C(4h) | 0.1029 | 0.3972 | 0.5 |
| **$Ti_3C_2$** | *P*4/*mbm* (Calc, Ref 1) | a=b=5.940,c=3.076 α=γ=90,β=144.898 | Ti(2a) | 0 | 0 | 0 |
| | | | Ti(4h) | 0.1579 | 0.6579 | 0.5 |
| | | | C(4g) | 0.1520 | 0.3480 | 0 |
| **$Ti_6C_5$** | *C*2/*m* | a=5.327,b=9.201,c=6.139 α=γ=90,β=125.202 | Ti(8j) | -0.0065 | -0.1752 | 0.2544 |
| | | | Ti(4i) | 0.0260 | -0.5 | 0.2632 |
| | | | C(2c) | 1.0 | 0 | 0.5 |
| | | | C(4h) | 1.0 | -0.3335 | 0.5 |
| | | | C(4g) | -0.5 | -0.1666 | 0 |
| **$Ti_6C_5$** | *C2/m* ( Calc, Ref 2) | a=5.234,b=9.066,c=5.234 α=γ=90,β=109.47 | Ti(8j) | 0.2410 | 0.1736 | 0.2462 |
| | | | Ti(4i) | 0.7603 | 0 | 0.2390 |
| | | | C(2a) | 0 | 0 | 0 |
| | | | C(4h) | 0 | 0.1665 | 0.5 |
| | | | C(4g) | 0 | 0.3332 | 0 |
| **TiC** | *Fm*-3*m* | a=b=c=4.336 | Ti(4a) | 0.5 | 0.5 | 0 |
| | | | C(4b) | 0.5 | 0 | 0 |
| **TiC** | *Fm*-3*m* (Exp, Ref 3) | a=b=c=4.328 | Ti(4a) | 0 | 0 | 0 |
| | | | C(4b) | 0.5 | 0.5 | 0.5 |
| **$TiC_2$** | *R*-3*m* | a=b=2.649,c=11.959 | Ti(3b) | 0.3333 | 0.6667 | 0.1667 |
| | | | C(6c) | 0 | 0 | 0.3137 |
| **$TiC_3$** | *R*-3*m* | a=b=2.603,c=30.670 | Ti(6c) | 0 | 0 | 0.1013 |
| | | | C(6c) | 0.6667 | 0.3333 | 0.3075 |
| | | | C(6c) | 0.6667 | 0.3333 | 0.1594 |
| | | | C(6c) | 0.3333 | 0.6667 | 0.0421 |
| **$TiC_4$** | *P*-3*m*1 | a=b=2.588,c=12.299 | Ti(2d) | 0.3333 | 0.6667 | 0.1633 |
| | | | C(2d) | 0.3333 | 0.6667 | 0.9818 |
| | | | C(2d) | 0.3333 | 0.6667 | 0.4796 |
| | | | C(2d) | 0.6667 | 0.3333 | 0.6473 |
| | | | C(2c) | 0 | 0 | 0.6893 |

**Ref 1**. C. Jiang and W. S. Jiang, Pressure–composition phase diagram of Ti–C from first principles, *Phys. Status Solidi B.*, 2014, **251,** 533–536.

**Ref 2**. P. A. Korzhavyi, L. V. Pourovskii, H. W. Hugosson, A. V. Ruban, and B. Johansson, Ab initio study of phase equilibria in TiC(x), *Phys. Rev. Lett.*, 2002, **88,** 015505.

**Ref 3**. G. Amirthan, K. Nakao, M. Balasubramanian, H. Tsuda and S. Mori, Influence of N and Fe on *α*-Ti precipitation in the in situ TiC–titanium alloy composites, *J. Mater. Sci.*, 2011, **46,** 1103-1109.

**Figure S2.** The curves of phonon dispersion for $TiC_n$ (n>1) compounds. $TiC_2$ (a) at 0 GPa, (b) at 100 GPa; $TiC_3$ (c) at 0 GPa, (d) at 100 GPa; $TiC_4$ (e) at 0 GPa, (f) at 100 GPa, respectively.

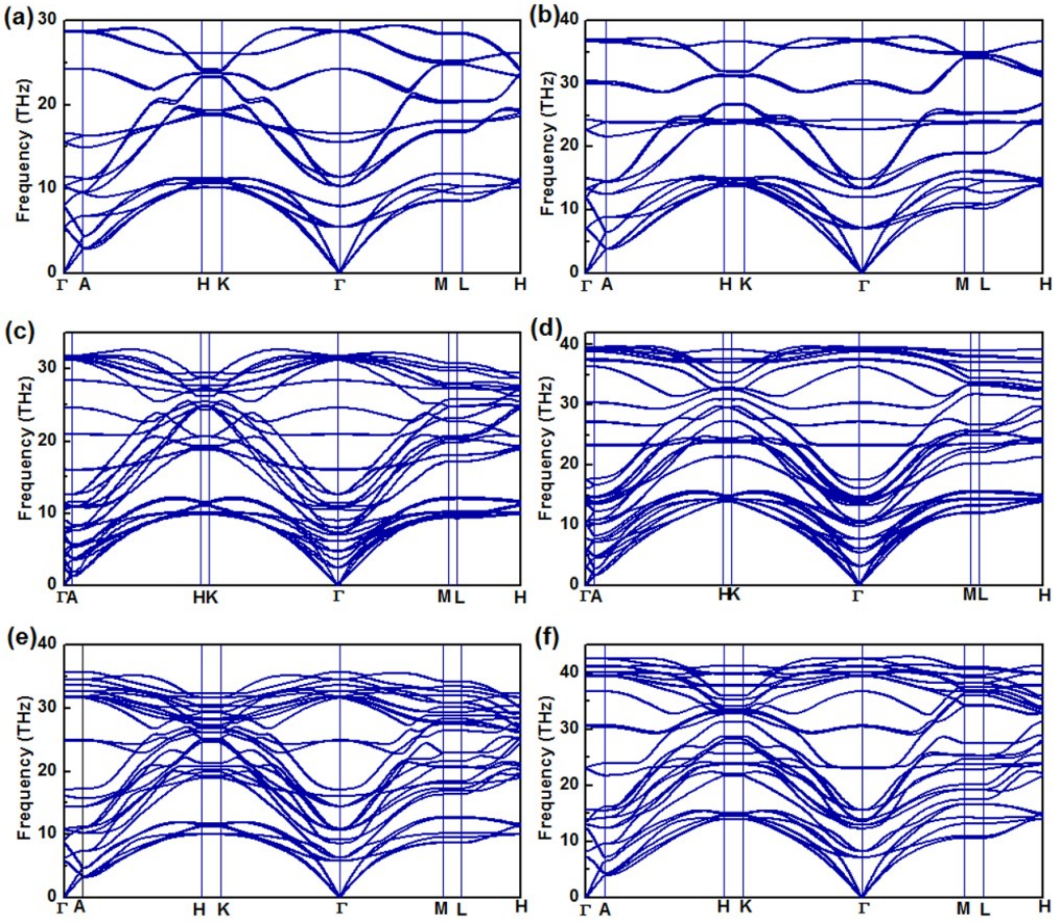

**Figure S3**. The calculated three-dimensional representations of linear compressibility, Poisson's ratio, shear ratio and Young's modulus for the TiC structure.

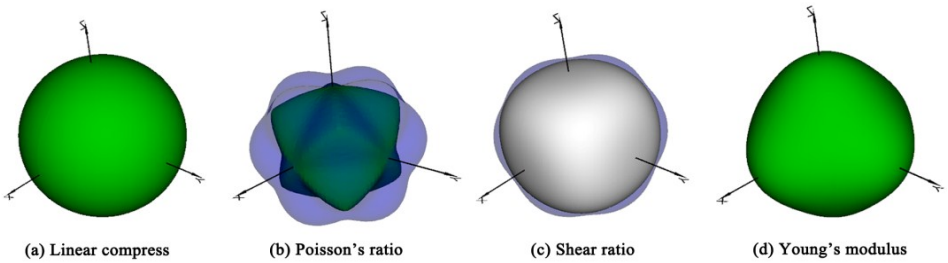


**Figure S4**. The calculated three-dimensional representations of linear compressibility, Poisson's ratio, shear ratio and Young's modulus for the $TiC_3$ structure.

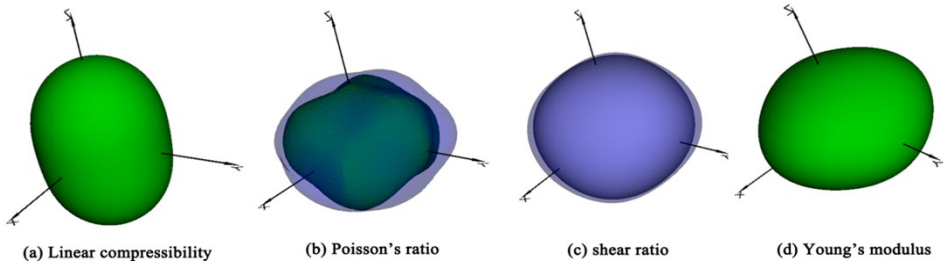


**Figure S5**. The calculated three-dimensional representations of linear compressibility, Poisson's ratio, shear ratio and Young's modulus for the $TiC_4$ structure.

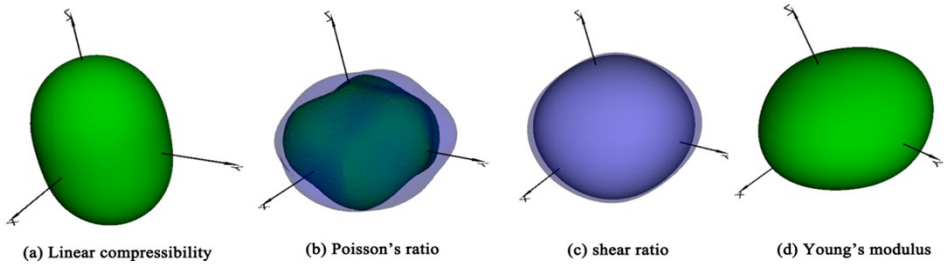


**Table S2.** The calculated formation enthalpies ΔH of $TMC_4$ (TM= V, Zr, Nb, Hf and Ta).

| | **$VC_4$** | **$ZrC_4$** | **$NbC_4$** | **$HfC_4$** | **$TaC_4$** |
|---|---|---|---|---|---|
| ΔH (eV/atom) | -0.46234 | -0.39428 | -0.17959 | -0.71717 | -0.14002 |

**Table S3.** Calculated elastic constants $C_{ij}$ (GPa), bulk modulus *B* (GPa), shear modulus *G* (GPa), Young's modulus Y (GPa), *B/G* and Poisson's ratio *v* of $TMC_4$ (TM= V, Zr, Nb, Hf and Ta).

| | $C_{11}$ | $C_{33}$ | $C_{44}$ | $C_{66}$ | $C_{12}$ | $C_{13}$ | ***B*** | ***G*** | ***Y*** | ***B/G*** | ***v*** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **$VC_4$** | 881 | 687 | 315 | 357 | 166 | 126 | 362 | 332 | 762 | 0.92 | 0.15 |
| **$ZrC_4$** | 720 | 623 | 269 | 298 | 125 | 102 | 301 | 282 | 645 | 1.07 | 0.14 |
| **$NbC_4$** | 727 | 567 | 264 | 265 | 197 | 172 | 342 | 256 | 615 | 0.75 | 0.20 |
| **$HfC_4$** | 739 | 632 | 272 | 304 | 131 | 96 | 305 | 288 | 656 | 1.06 | 0.14 |
| **$TaC_4$** | 736 | 576 | 255 | 273 | 190 | 174 | 345 | 257 | 617 | 0.74 | 0.20 |

**Figure S6.** The curves of phonon dispersion for $TMC_4$ (TM= V, Zr, Nb, Hf and Ta) at ambient pressure. (a) $VC_4$, (b) $ZrC_4$, (c) $NbC_4$, (d) $HfC_4$ and (e) $TaC_4$.

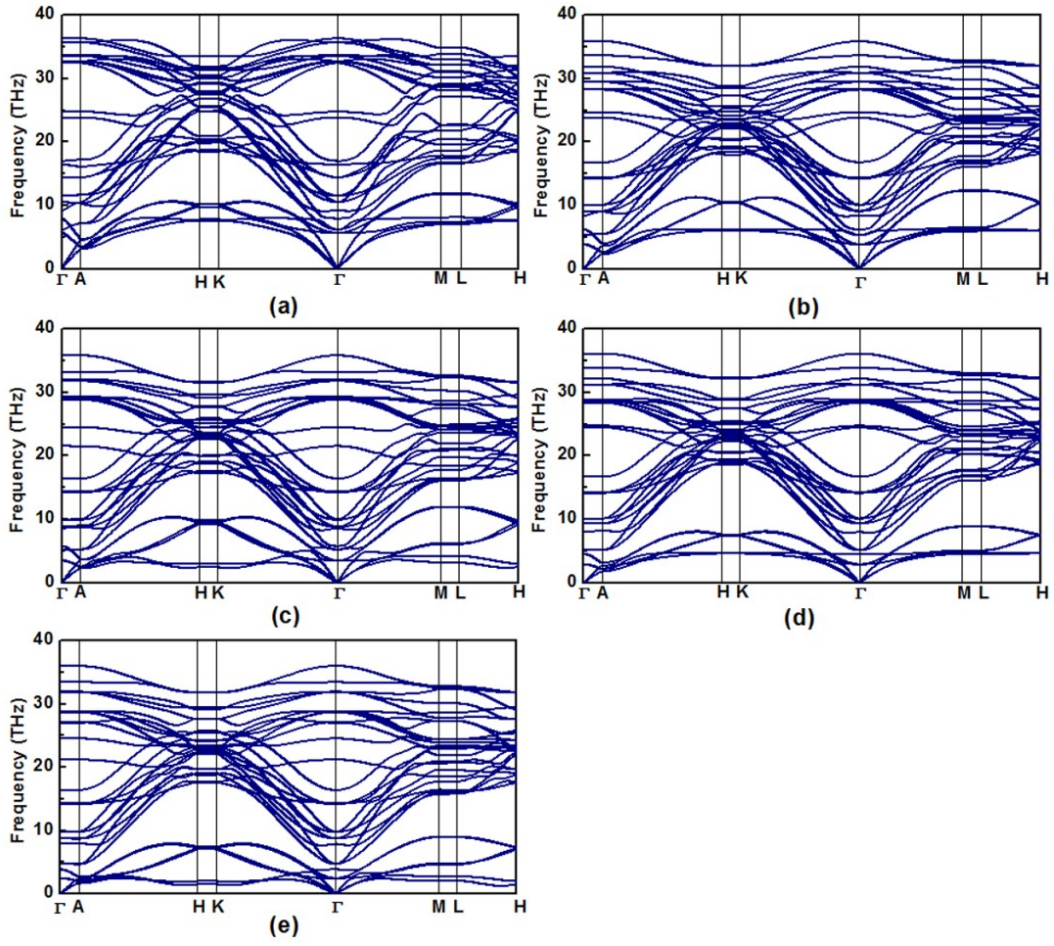

**Table S4.** The optimized lattices parameters and atomic coordinates of $TMC_4$ (TM= V, Zr, Nb, Hf and Ta) at ambient pressure.

| | Space Group | Lattice Parameters ( Å ) | Atoms | x | y | z |
|---|---|---|---|---|---|---|
| **$VC_4$** | *P*-3*m*1 | a=b=2.5600,c=12.0099 | C (2d) | 0.66667 | 0.33333 | 0.52106 |
| | | | C (2d) | 0.66667 | 0.33333 | 0.01867 |
| | | | C (2d) | 0.33333 | 0.66667 | 0.34908 |
| | | | C (2c) | 0 | 0 | 0.69451 |
| | | | V (2d) | 0.66667 | 0.33333 | 0.84012 |
| **$ZrC_4$** | *P*-3*m*1 | a=b=2.6833,c=13.0102 | C(2d) | 0.66667 | 0.33333 | 0.51939 |
| | | | C (2d) | 0.66667 | 0.33333 | 0.01657 |
| | | | C (2d) | 0.66667 | 0.33333 | 0.36162 |
| | | | C (2c) | 0 | 0 | 0.67810 |
| | | | Zr (2d) | 0.66667 | 0.33333 | 0.83111 |
| **$NbC_4$** | *P*-3*m*1 | a=b=2.6529,c=12.7689 | C (2d) | 0.66667 | 0.33333 | 0.51979 |
| | | | C (2d) | 0.66667 | 0.33333 | 0.01824 |
| | | | C (2d) | 0.33333 | 0.66667 | 0.35865 |
| | | | C (2c) | 0 | 0 | 0.68201 |
| | | | Nb (2d) | 0.66667 | 0.33333 | 0.83333 |
| **$HfC_4$** | *P*-3*m*1 | a=b=2.6740,c=12.8550 | C (2d) | 0.66667 | 0.33333 | 0.51966 |
| | | | C (2d) | 0.66667 | 0.33333 | 0.01780 |
| | | | C (2d) | 0.33333 | 0.66667 | 0.36005 |
| | | | C (2c) | 0 | 0 | 0.68065 |
| | | | Hf (2d) | 0.66667 | 0.33333 | 0.83245 |
| **$TaC_4$** | *P*-3*m*1 | a=b=2.6577,c=12.7097 | C (2d) | 0.66667 | 0.33333 | 0.51992 |
| | | | C (2d) | 0.66667 | 0.33333 | 0.01958 |
| | | | C (2d) | 0.66667 | 0.33333 | 0.35818 |

| | | | | |
|---|---|---|---|---|
| C (2c) | 0 | 0 | 0.68322 | |
| Ta (2d) | 0.66667 | 0.33333 | 0.83424 | |

**Table S5.** Calculated bond parameters and Vicker hardness of $TMC_4$(TM= V, Zr, Nb, Hf and Ta) structures.

| Crystals | bond type | $d^{\mu}$(Å) | $v_b^{\mu}$(Å$^3$) | $P$ | $f_m$ | $H_{v\ Gao}$ (GPa) |
|---|---|---|---|---|---|---|
| VC4 | C-C | 1.544 | 1.296 | 0.90 | | 50.3 |
| | C-C | 1.560 | 1.337 | 0.79 | | |
| | C-C | 1.562 | 1.342 | 0.87 | | |
| | C-C | 1.568 | 1.357 | 0.88 | | |
| | V-C | 2.250 | 4.011 | 0.08 | 1.157×10-3 | |
| | V-C | 2.290 | 4.228 | 0.08 | 1.157×10-3 | |
| **$ZrC_4$** | C-C | 1.548 | 1.202 | 0.80 | | 41.9 |
| | C-C | 1.609 | 1.350 | 0.85 | | |
| | C-C | 1.630 | 1.404 | 0.83 | | |
| | C-C | 1.634 | 1.414 | 0.83 | | |
| | Zr-C | 2.514 | 5.149 | 0.08 | $1.848\times10^{-4}$ | |
| | Zr-C | 2.519 | 5.180 | 0.08 | $1.848\times10^{-4}$ | |
| **$NbC_4$** | C-C | 1.554 | 1.249 | 0.80 | | 43.9 |
| | C-C | 1.605 | 1.376 | 0.84 | | |
| | C-C | 1.613 | 1.397 | 0.84 | | |
| | C-C | 1.618 | 1.410 | 0.85 | | |
| | Nb-C | 2.431 | 4.783 | 0.09 | $1.054\times10^{-3}$ | |
| | Nb-C | 2.463 | 4.974 | 0.08 | $1.054\times10^{-3}$ | |
| **$HfC_4$** | | | | | | |
| | C-C | 1.527 | 1.616 | 0.79 | | 49.3 |
| | C-C | 1.608 | 1.356 | 0.86 | | |
| | C-C | 1.622 | 1.391 | 0.83 | | |
| | C-C | 1.627 | 1.404 | 0.84 | | |
| | Hf-C | 2.484 | 5.688 | 0.12 | $3.907\times10^{-4}$ | |

| | | | | | | |
|---|---|---|---|---|---|---|
| | Hf-C | 2.502 | 5.106 | 0.12 | $3.907\times10^{-4}$ | |
| **$TaC_4$** | C-C | 1.527 | 1.178 | 0.80 | | 59.2 |
| | C-C | 1.604 | 1.365 | 0.83 | | |
| | C-C | 1.613 | 1.388 | 0.83 | | |
| | C-C | 1.618 | 1.401 | 0.84 | | |
| | Ta-C | 2.441 | 4.810 | 0.17 | $1.228\times10^{-3}$ | |
| | Ta-C | 2.469 | 4.978 | 0.16 | $1.228\times10^{-3}$ | |

**Table S6.** The different bond length d (Å) within the Ti-C and C-C bonds and their corresponding integrated crystal orbital Hamiltonian population values ((-ICOHP, eV per bond).

| | **Bond** | ***d*** | **ICOHP** |
|---|---|---|---|
| **TiC** | Ti-C1 | 2.168 | 2.99 |
| **$TiC_2$** | Ti-C1 | 2.228 | 1.42 |
| | Ti-C1 | 2.331 | 1.55 |
| | C1-C1 | 1.600 | 8.65 |
| **$TiC_3$** | Ti-C2 | 2.228 | 1.42 |
| | Ti-C1 | 2.315 | 0.97 |
| | Ti-C2 | 2.329 | 1.50 |
| | Ti-C3 | 2.357 | 1.54 |
| | C1-C1 | 1.586 | 8.39 |
| | C2-C2 | 1.568 | 9.12 |
| | C1-C3 | 1.584 | 9.06 |
| **$TiC_4$** | Ti-C1 | 2.232 | 1.40 |
| | Ti-C1 | 2.328 | 1.49 |
| | Ti-C3 | 2.330 | 0.90 |
| | Ti-C4 | 2.350 | 1.58 |
| | C1-C1 | 1.559 | 9.26 |
| | C2-C2 | 1.576 | 9.22 |
| | C3-C4 | 1.560 | 9.11 |

| | | | |
|---|---|---|---|
| | C3-C4 | 1.581 | 9.05 |

**Table S7.** Bader charge analysis using supercell calculations 2×2×2 of TiC, 2×2×2 of $TiC_2$, 2×2×1 of $TiC_3$ and 2×2×2 of $TiC_4$ at ambient pressure.

| Structure | Atom (Number) | Charge value (e) | δ(e) |
|---|---|---|---|
| TiC | Ti (32) | 8.34 | 1.66 |
| | C (32) | 5.66 | -1.66 |
| $TiC_2$ | Ti (24) | 8.99 | 1.01 |
| | C (24) | 4.50 | -0.50 |
| | C (24) | 4.51 | -0.51 |
| $TiC_3$ | Ti (24) | 9.01 | 0.99 |
| | C (12) | 4.02 | -0.02 |
| | C (12) | 4.06 | -0.06 |
| | C (24) | 4.46 | -0.46 |
| | C(9) | 4.48 | -0.48 |
| | C (15) | 4.49 | -0.49 |
| $TiC_4$ | Ti (16) | 9.01 | 0.99 |
| | C(8) | 3.99 | 0.01 |
| | C (8) | 4.49 | -0.49 |
| | C (8) | 4.00 | 0 |
| | C(16) | 4.03 | -0.03 |
| | C (24) | 4.48 | -0.48 |