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# Carbon-rich superhard ruthenium carbides from first-principles

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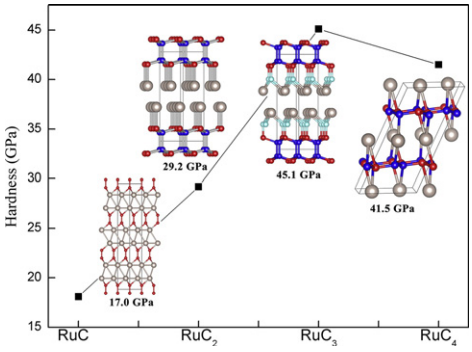
## HIGHLIGHTS

- Ruthenium carbides with various stoichiometries were studied by density functional theory calculations.
- Ground states of $Ru_2C$, RuC, $Ru_2C_3$, $RuC_2$, $RuC_3$ and $RuC_4$ are found, pressure-induced phase transitions are uncovered.
- Two carbon-rich structures are found to have large Vickers hardness 45.1 GPa and 41.5 GPa.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Compounds formed by transition metals and light elements have attracted increasing attention owing to superior functionalities. Here, high throughput first-principles calculations are employed to investigate the crystal structures and physical properties of ruthenium carbides with various stoichiometries. It is found that the $R\bar{3}m$-$Ru_2C$, $R\bar{3}m$-RuC, $P\bar{3}m1$-$Ru_2C_3$, $P\bar{3}m1$-$RuC_2$, $P\bar{3}m1$-$RuC_3$ and $C2/c$-$RuC_4$ are the ground states for the respective chemical compositions at ambient pressure, from a systematical investigation of both thermodynamic and mechanical stabilities, as well as phonon dispersions. Further calculations indicate that $P\bar{3}m1$-$RuC_3$ and $P6_3/mmc$-$RuC_4$ are ultra-incompressible with high bulk and shear modulus. Subsequent empirical calculations predict that the carbon-rich $P\bar{3}m1$-$RuC_3$ and $P6_3/mmc$-$RuC_4$ are *superhard* materials with a large Vickers hardness of 45.1 GPa and 41.5 GPa, respectively. In addition, a strong covalent C—C bonding was observed from the electronic localization function contours of all the ground states, which is crucial for their excellent mechanical properties.



## 1. Introduction

Superhard materials are widely used in machining, wear-resistant coating and abrasive due to their high stiffness, high hardness, high melting point, good thermal conductivity and excellent corrosion resistance [1,2]. The first generation superhard materials are mainly composed of light elements (like B, C, N and O) with strong covalent bonds, e.g. $C_3N$ [3], $BC_3$ [4], $B_3N_5$ [5] etc. In recent years, another series of compounds formed by light elements and transition metals (TM), like W, Tc, Re, Ru, Os and Ir, have attracted increasing attention and are considered as the potential superhard materials with good

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mechanical properties [6–11]. TM carbides are considered as candidates for hard or superhard materials, such as Os-C [1,12], W-C [13,14], Tc-C [7,15] and Re-C [16] systems in which the arrangement of the carbon atoms plays an important role in the mechanical properties of these carbides. The systematical first principles investigation can offer a guidance to enhance the mechanical properties by optimizing the carbon concentrations in the TM carbides.

RuC with a hexagonal WC-type (space group $P\bar{6}m2$) structure was first synthesized at ambient pressure and high temperature in 1960 [17,18]. Recently, Tian et al. [19] studied the structures and stabilities of ten typical *AB*-type ruthenium monocarbide. The zinc-blend (ZB) structure was claimed to be energetically more stable than others at ambient condition. Zhao et al. [20] investigated the stability and phase transition of RuC by first-principles calculations, and showed that the ZB-type RuC was stable at lower pressure and transformed to a WC-type structure at 20 GPa. Hao and co-workers [21] studied the ZB-type, WC-type, and OsC-type ($Pmn2_1$) RuC. They found that the $Pmn2_1$ structure would change to a tetrahedral *I*4*mm* structure after full optimization and was more stable in 9.3–26 GPa. However, the ZB-type structure remained the most stable below 9.3 GPa among these studied phases. Later, the crystal structure of RuC was explored using the particle swarm optimization algorithm by Zhang et al. [22]. In contrast to the

**Table 1**
Optimized equilibrium lattice parameters *a*, *b* and *c* (Å); Formation Enthalpies $E_f$ (eV) at ambient pressure of ruthenium carbides with various stoichiometries.

| | Structure | Space group | *a* | *b* | *c* | $E_f$ |
|---|---|---|---|---|---|---|
| $Ru_2C$ | $Ru_2C$ | $P\bar{3}m1$ | 2.82 (2.88[a], 2.81[b], 2.82[c]) | | 5.01 (4.88[a], 4.98[b], 5.01[c]) | 1.50 |
| | $Ru_2Si$ | *Pnma* | 5.38 | 3.95 | 6.42 | 1.31 |
| | $Ru_2C$ | $P6_3/mmc$ | 2.77 (2.77[c]) | | 10.21 (10.21[c]) | 1.10 |
| | $Ru_2C$ | *R*3*m* | 2.78 (2.77[d]) | | 15.13 (15.14[d]) | 1.05 |
| | $Re_2P$ | *Pnma* | 5.13 | 2.78 | 9.65 | 1.05 |
| | $Re_2N$ | $P6_3/mmc$ | 2.79 | | 10.04 | 1.02 |
| | $Pd_2B$ | *Pnnm* | 4.95 | 4.80 | 2.93 | 0.98 |
| | $W_2C$ | *Pbcn* | 4.96 | 5.64 | 5.00 | 0.92 |
| | $Ru_2C$ | $P\bar{3}1m$ | 4.93 (4.93[c]) | | 4.98 (4.98[c]) | 0.90 |
| | $Ru_2C$ | $R\bar{3}m$ | 2.76 (2.76[d]) | | 31.56 (31.50[d]) | 0.74 |
| RuC | CsCl | $Pm\bar{3}m$ | 2.67 | | | 2.25 |
| | CrB | *Cmcm* | 4.18 | 7.45 | 2.61 | 1.62 |
| | TiB | *Pnma* | 6.40 | 2.63 | 4.84 | 1.45 |
| | NiAs | $P6_3/mmc$ | 2.93 | | 5.41 | 1.25 |
| | WC | $P\bar{6}m2$ | 2.94 (2.91[e],2.92[f]) | | 2.68 (2.82[e], 2.67[f]) | 1.20 |
| | RuC | *I*4*mm* | 2.82 (2.85[g]) | | 5.35 (5.36[g]) | 1.00 |
| | ZnS | $F\bar{4}3m$ | 4.57 (4.55[f]) | | | 0.86 |
| | RuC | $R\bar{3}m$ | 2.78 (2.79[h]) | | 18.92 (18.89[h]) | 0.64 |
| $Ru_2C_3$ | $W_2B_3$ | *Imm*2 | 2.59 | 7.22 | 5.20 | 5.48 |
| | $Ru_2Ge_3$ | $P\bar{4}c2$ | 4.98 | | 7.83 | 5.40 |
| | $Cr_2O_3$ | $R\bar{3}c$ | 4.86 | | 15.65 | 4.80 |
| | $Ru_2Si_3$ | *Pbcn* | 10.84 | 7.26 | 5.12 | 4.47 |
| | $Y_2O_3$ | $P\bar{3}m1$ | 2.70 | | 7.46 | 3.11 |
| $RuC_2$ | $RuN_2$ | *P*4/*mbm* | 4.46 | | 2.65 | 3.28 |
| | $IrN_2$ | $P2_1/c$ | 4.70 | 5.21 | 4.55 | 2.66 |
| | $OsN_2$ | *Pnnm* | 4.54 | 4.46 | 2.78 | 2.64 |
| | $OsSi_2$ | *Cmca* | 7.22 | 5.32 | 11.87 | 2.40 |
| | $OsGe_2$ | *C*2/*m* | 8.34 | 2.68 | 6.91 | 1.86 |
| | $RuSi_2$ | *Cmca* | 7.62 | 8.60 | 7.26 | 1.79 |
| | $OsC_2$ | $P\bar{6}m2$ | 2.86 | | 4.00 | 1.56 |
| | $MoB_2$ | $R\bar{3}m$ | 2.53 | | 39.68 | 1.53 |
| | $OsC_2$ | $P6_3/mmc$ | 2.85 | | 8.00 | 1.52 |
| | $OsB_2$ | *Pmmn* | 4.27 | 2.54 | 5.43 | 1.38 |
| | $OsC_2$ | $P\bar{3}m1$ | 2.59 | | 9.01 | 1.19 |
| $RuC_3$ | $WB_3$ | $P\bar{6}m2$ | 3.21 | | 4.09 | 8.11 |
| | $CrB_3$ | *Pmmm* | 249 | 2.89 | 4.68 | 7.28 |
| | $RuP_3$ | $P\bar{1}$ | 4.57 | 5.34 | 6.45 | 2.71 |
| | $WB_3$ | $P6_3/mmc$ | 4.21 | | 16.83 | 2.39 |
| | $WB_3$ | $R\bar{3}m$ | 4.20 | | 24.87 | 2.36 |
| | $TcP_3$ | *Pnma* | 15.10 | 2.63 | 3.97 | 2.10 |
| | $OsC_3$ | $P\bar{3}m1$ | 2.67 | | 10.56 | 1.16 |
| $RuC_4$ | $IrGe_4$ | $P3_121$ | 4.95 | | 5.77 | 6.28 |
| | $OsB_4$ | *Pmmn* | 8.55 | 2.62 | 3.60 | 4.82 |
| | $FeP_4$ | $C222_1$ | 4.21 | 9.38 | 4.15 | 4.06 |
| | $ReB_4$ | *C*2/*m* | 6.50 | 2.56 | 10.28 | 3.24 |
| | $ReP_4$ | *Pbca* | 4.83 | 7.67 | 9.21 | 3.19 |
| | $PtSn_4$ | *Ccca* | 4.32 | 8.86 | 4.91 | 2.60 |
| | $MoB_4$ | $P6_3/mmc$ | 2.71 | | 12.35 | 2.46 |
| | $OsO_4$ | *C*2/*c* | 9.53 | 5.02 | 4.45 | 2.28 |

[a] Ref. [23].
[b] Ref. [24].
[c] Ref. [25].
[d] Ref. [26].
[e] Ref. [17].
[f] Ref. [19].
[g] Ref. [21].
[h] Ref. [22].