Structural, mechanical and electronic properties of Nb₂C: first-principles calculations†

Xiaojing Sha, Namin Xiao, Yongjun Guan and Xiaosu Yi*

Nb–C compounds are potential candidates to achieve high hardness and refractory nature. We performed a crystal structure search for the Nb–C system using an ab initio evolutionary algorithm implemented in the USPEX code. By comparing the formation enthalpy, a P–x phase diagram was calculated, and an orthorhombic Pnmm structure of Nb₂C was predicted and denoted as Nb₂C-I, which was both mechanically and dynamically stable. In this Pnmm phase, there are four-sided rings continuously along the c-axis, which probably contributes to the relatively high incompressibility of Nb₂C-I along the crystallographic c-axis. Moreover, the hardness and Young’s modulus were calculated to be 28.5 GPa and 448.9 GPa, respectively; hence, the Nb₂C-I is considered as a potential ultra-stiff and hard material.

Therefore, the type of TM-LE bonding is the key factor for improving the hardness. Due to the behavior of high valence electron density and large interatomic distance, the transition metal can be intercalated with light elements, which may lead to the formation of covalent bonding between light elements and transition metals. Thus, the relatively high directional covalent bonds and valence electron density are considered to favor the formation of new superhard materials. It is believed that the carbides of the group-IV, -V, and -VI transition metals show an unusual combination of physical and chemical properties. The transition-metal carbide (TMC) compounds combine the physical properties of three different kinds of materials; transition metals, covalent solids and ionic crystals, making TMC a family of industrially relevant compounds with outstanding physical properties.

The niobium carbides are an emblematical TMC system, which exhibits meaningful physicochemical properties. Moreover, niobium carbides are significant candidates for improving the mechanical properties of niobium alloys. Niobium and carbide could form weak metallic or semiconductors compounds with different compositions and space symmetries. In the Nb–C binary phase diagram, niobium carbides have four experimentally known compositions: NbC, Nb₅C₃, Nb₃C₁₇, and Nb₂C. Stoichiometric NbC is in the rocksalt structure, in which Nb atoms form the cubic lattices, and C atoms occupy the octahedral interstitial positions. Nb₄C₃ was reported to adopt a R3m space group, and Nb₅C₃ is in the P3₁ space group. Among all the niobium carbides, NbC is the least understood carbide; it exists in three polymorphic forms: γ-Nb₂C, β-Nb₂C, and α-Nb₂C as reported in previous studies. The γ- and β-Nb₂C are hexagonal phases. The γ-Nb₂C is in L1₃-type structure at temperatures above 2770 K. The β-Nb₂C has ζ-, η-, Fe₂N structure at relatively low temperatures. The α-Nb₂C is an orthorhombic low temperature phase. As Hugosson reported,
some controversy exists in the determination of the structure of the orthorhombic phase. In his study, both structures showed energies of formation higher than those of the hexagonal phase. However, other studies showed that the formation energy of $\alpha$-Nb$_2$C was the lowest, which indicated that the formation of $\alpha$-Nb$_2$C was feasible.\textsuperscript{28,32} To date, controversy still remains regarding the orthorhombic phase structure of Nb$_2$C.

In this article, we performed a crystal structure search for the Nb–C system using an \textit{ab initio} evolutionary algorithm implemented in the USPEX code. Full $P-x$ phase diagrams of the Nb–C system at 0 K were calculated. We report a new phase for Nb$_2$C at high pressures. The predicted new phase of Nb$_2$C belongs to the orthorhombic $Pnma$ space group. Moreover, this phase is dynamically and mechanically stable at ambient and high pressures. Through a detailed electronic structure analysis, we found that niobium and carbon formed strong bonds with $sp^3$ hybridization style, which further knitted into three-dimensional networks. Collectively, we proved that Nb$_2$C can be a potential candidate for an ultra-stiff and hard material.

2 Methods

To search the stable and low-enthalpy structures of the Nb–C system, the evolutionary algorithm USPEX\textsuperscript{24–30} coupled with an \textit{ab initio} evolutionary algorithm (EA) was employed. The calculation was designed to find the most stable structure for the given stoichiometries under given external conditions as implemented in the USPEX code. In this study, evolutionary crystal structure prediction calculations were performed at 0, 10, 30, and 50 GPa for the Nb$_x$C$_y$ system ($x = 1–8, y = 1–8$) at zero temperature. We performed \textit{ab initio} calculations with the local density approximation (LDA), as implemented in the Vienna \textit{ab initio} simulation package (VASP) code,\textsuperscript{36–37} which is based on density functional theory. The electron–ion interaction was described via the projector augmented wave (PAW) scheme.\textsuperscript{38} The orbitals 2s and 2p for C and 4p, 4d, and 5s for Nb were treated as valence states. During structural relaxation, a tested energy cutoff of 600 eV was used for the plane wave basis sets, and Monkhorst–Pack\textsuperscript{39} $k$-point meshes with a resolution of 0.03 Å$^{-1}$ in the reciprocal space were used for all structures to minimize error from the $k$-point meshes. The atomic positions, lattice parameters, and cell volume were fully relaxed until the force on each atom was less than 1 meV Å$^{-1}$. Phonons were calculated using the supercell method implemented in the PHONOPY package.\textsuperscript{40,41} The strain–stress method was used to calculate the elastic constants. The shear modulus, bulk modulus, Young’s modulus, and Pugh’s indicator were derived from the Voigt–Reuss–Hill approximation.\textsuperscript{42–44} The structure diagram of Nb$_2$C was drawn using VESTA.\textsuperscript{45}

3 Results and discussion

In this study, we uncovered a stable structure of Nb$_2$C, denoted as Nb$_2$C-I. At first, we calculated the formation enthalpy of Nb$_x$C$_{1-x}$ using a fractional representation of Nb$_x$C$_{1-x}$ with respect to its decomposition into Nb and C as

$$\Delta H(Nb_xC_{1-x}) = H(Nb_xC_{1-x}) - [x \times H(Nb) + (1-x) \times H(C)]$$

where $x$ is the concentration of Nb. The formation enthalpies from 0 to 50 GPa were evaluated as the difference in the enthalpy of the predicted Nb–C system with respect to Nb metal and C in their most stable forms (bcc phase for Nb and graphite for C), as depicted in Fig. 1. The formation enthalpy of NbC
calculated against decomposition into Nb$_6$C$_5$ and C; thus, we shown in the ESI Fig. S1(a), if the pressure is increased to 50 GPa. The structure with high carbon concentration is not stable, even appear and decompose with the increase of pressure. However, the cubic phase. Moreover, some phases of niobium carbides rhombic to monoclinic transition and then transforms back to C concentration, the Nb was constructed, which is plotted in Fig. 3. With the increase in pressure \( \frac{C}{P} \) \( \frac{C}{P} \) \( \frac{C}{P} \) respectively. With these detailed calculations shown in Fig. S1,† the enthalpy difference of NbC is calculated against decomposition into Nb$_6$C$_5$ and C; thus, we concluded that the NbC phase becomes stable at 12.3 GPa. The enthalpy differences of Nb$_6$C$_5$ and Nb$_2$C-\( Pnnm \) are calculated against decomposition into the constituent carbides. As shown in Fig. S1(b) and (c), the structures of Nb$_4$C$_3$ and Nb$_2$C-\( Pnnm \) become completely unstable at 39.7 GPa and 40.5 GPa, respectively. With these detailed calculations shown in Fig. S1,† a pressure–constituent (\( P-x \)) phase diagram of niobium carbide was constructed, which is plotted in Fig. 3. With the increase in C concentration, the Nb–C system first undergoes an orthorhombic to monoclinic transition and then transforms back to the cubic phase. Moreover, some phases of niobium carbides appear and decompose with the increase of pressure. However, the structure with high carbon concentration is not stable, even if the pressure is increased to 50 GPa.

The \( Pnnm \) structure, as we predicted, contains two Nb$_2$C in a unit cell at 20 GPa (\( a = 5.415 \text{ Å} \), \( b = 4.837 \text{ Å} \), and \( c = 3.019 \text{ Å} \)), in which two inequivalent atoms Nb and C occupy the Wyckoff 8h (0.3462, 0.7632, 0.5000) and 2b (0.5, 0.5, 0.0) sites, as summarized in Table 1 and shown in Fig. 4. Fig. 4(b) along the \( y \)-axis and Fig. 4(c) along the \( z \)-axis reveal a fundamental structure in the \( Pnnm \) phase. Fig. 4(d) shows the structure of \( Pnnm \) phase along the \( y \)-axis. When we compared Fig. 4(b) with (d), it was observed that the carbon atoms in Nb$_2$C-\( Pnnm \) could help to achieve better formation of the three-dimensional space grid structure, which avoided the appearance of the interaction between metal atoms.

It is well-known that the phonon dispersion curves give information about the global structural stability of the materials. As shown in Fig. 5, we analyzed the phonon dispersion curves to test the lattice dynamical stability of Nb$_2$C-\( I \) at 0 and 20 GPa. The calculated phonon curves of Nb$_2$C have no soft mode in the Brillouin zone, indicating that Nb$_2$C is dynamically stable. For the purpose of understanding the mechanical properties, the elastic constants are deemed essential. The elastic constants \( C_{ij} \) of the \( Pnnm \) phases are listed in Table 2. For the proposed Nb$_2$C-\( Pnnm \), all \( C_{ij} \) satisfy Born–Huang criteria, which means that the proposed Nb$_2$C-\( Pnnm \) is mechanically stable. We determined that the Nb$_2$C-\( Pnnm \) could be synthesized under high pressure and preserved under ambient pressure. From Table 2, it can be found that the calculated \( C_{33} \) value is bigger than the values of \( C_{11} \) and \( C_{22} \), indicating that there is relatively high incompressibility along the \( c \)-axis. The relative high incompressibility of the proposed Nb$_2$C along the \( c \)-axis is perhaps contributed by the existence of four-sided rings, which are continuously along the crystallographic \( c \)-axis. In contrast, four-sided rings and eight-sided rings exist alternately along the \( b \)-axis or \( c \)-axis. Therefore, there is certain disparity between \( C_{13} \) and \( C_{11} \) (or \( C_{22} \)).

It is well-known that superhard materials should have high bulk modulus and high shear modulus to resist the volume change and shape change. At 0 and 20 GPa, the bulk modulus of Nb$_2$C-\( Pnnm \) is 244 and 310 GPa, respectively, which are larger than the values of Nb$_2$C-\( Pnnma \) (236 and 304 GPa, respectively). Because the value of the bulk modulus is large, Nb$_2$C can be grouped into incompressible materials. As reported in Table 2,
The Poisson’s ratio $\nu$ of Nb$_2$C-Pnmm is about 0.19. Usually, strong directionality degree of covalent bonding is considered in the materials when the $\nu$ value is near 0.2, indicating that the directionality degree of covalent bonding of Nb$_2$C-Pnmm is strong. The Pugh’s indicator $\frac{G}{B}$ of Nb$_2$C is 0.77, which is a relatively large value. According to the Pugh’s modulus ratio defined by Cheng et al.,$^{47}$ the Nb$_2$C-I phase is a brittle and hard material with a huge capability to resist elastic plastic deformation. To gain a more comprehensive and profound understanding of the mechanical property, we calculated the Vickers hardness of Nb$_2$C-I. The Vickers hardness $H_V$ estimated by the empirical model, was obtained by the following formula:

$$H_V = (k^2G)^{0.585} - 3 (k = \frac{G}{B})$$

The calculated hardness of Nb$_2$C-I is 28.5 GPa, which almost matches that of the hard material WC (21.5–33.4 GPa).$^{47,48}$ Our results suggested that the proposed Nb$_2$C-I could be a potential candidate for ultra-stiff and hard materials.

The electronic structure is crucial to understand the origin of physical properties of these carbides. The total and site projected electronic densities of states (PDOS) of Nb$_2$C-I are shown in Fig. 6(a). As the graphic shows, Nb$_2$C is a metal as the d electronics of Nb are mainly attributed to the density near the Fermi energy in our calculation model. To determine the hybridization between C and Nb, projected electronic densities of states of the nearest Nb and C are calculated, as shown in Fig. 6(b). There is an obvious hybridization between C 2p and Nb 4d states, which is a common feature of typical TMC superhard materials. To obtain more information about the bonding character, the electronic localization function (ELF) of Nb$_2$C-I was calculated, as shown in Fig. 7. The electron localization function between Nb atoms and C atoms has a slight increase as compared to that in the background, which

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<th>Table 1</th>
<th>The optimized equilibrium lattice constants $a$, $b$, and $c$ (Å), and atomic coordinates for Nb$_2$C-I at 20 GPa</th>
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<tr>
<td>Structure</td>
<td>Parameters (Å)</td>
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<td>Nb$_2$C</td>
<td>$Pnmm$ (orthorhombic) $a = 5.415, b = 4.837, c = 3.019$</td>
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Fig. 4  Crystal structures of the predicted Nb$_2$C-Pnmm. (a) The structure of Nb$_2$C-Pnmm. (b) The structure along the y-axis. (c) Along the z-axis. The large gray and small blue spheres represent the Nb and C atoms, respectively. (d) The structure of Nb$_2$C-Pnma along the y-axis.
indicates that mixed bonds between the two atoms are present in this area, in which the ionic bonds are dominant. As Becke defined, the electrons can move freely in the areas of ELF = 0.5. In Fig. 7(a), the green region is almost connected. However, there are disconnected equivalent spheres in Fig. 7(b). In total, the equivalent sphere of ELF = 0.5 is partially connected in the whole crystal, which may enhance the weak metallicity properties.

4 Summary

In summary, we researched the full-scale zero-temperature Nb–C phase diagram using an ab initio evolutionary algorithm implemented in the USPEX code. The P–x phase diagrams of the Nb–C system are constructed. A new structure of Nb2C has been uncovered and denoted as Nb2C-I. The Nb2C-I belongs to the orthorhombic system with the space group Pnnm. Phase stability, mechanical properties, and electronic properties of Nb2C-I were investigated. The Vickers hardness and Young’s modulus of Nb2C-I have been calculated to be 28.5 GPa and 448.9 GPa, respectively, which prove that Nb2C-I can be considered as low compressible materials. We considered that the formation of continuous four-sided rings along the c-axis might cause high incompressibility of Nb2C-I in the c-axis direction. A deep analysis of the electronic density of states and chemical bonding indicates that an ionic bond is dominant in the Nb2C crystals.

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References