Structural, mechanical and electronic properties of Nb$_2$C: first-principles calculations†

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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 Pnnm structure of Nb$_2$C was predicted and denoted as Nb$_2$C-I, which was both mechanically and dynamically stable. In this Pnnm phase, there are four-sided rings continuously along the c-axis, which probably contributes to the relatively high incompressibility of Nb$_2$C-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 Nb$_2$C-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 exhibit meaningful physicochemical properties. Therefore, development of novel superhard multifunctional materials is an urgent requirement.

During the past decade, scientists were focused on the design of new materials in transition-metal (TM) light-element (LE) systems. One of the advantages of transition metals is their large bulk modulus. For example, the bulk modulus of Os is about 395–462 GPa, which is close to that of diamond (446 GPa). However, the hardness of metal is always low, which is normally one-thirtieth that of diamond. This is mainly due to the huge difference of chemical bonds in the compound structures. Classical superhard materials usually hold three-dimensional networks composed of covalent bonds with sp$^3$ hybridization, which is the basis of superhard properties.

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1 Introduction

In the past few decades, superhard materials with excellent mechanical properties have drawn extensive attention from the researchers and have been well-studied in terms of both theoretical and experimental aspects. Traditional superhard materials, such as diamond, $\gamma$-B, $\alpha$-BN, and c-BC$_2$N, are mainly composed of light elements. Diamond, the earliest discovered superhard material, shows promising mechanical properties and is hence among the most widely used superhard materials. However, diamond shows its own practical defects. At a temperature greater than 800 °C, diamond tends to oxidize. Moreover, when the diamond tool is used in the grinding or cutting of ferrous materials, the tool easily reacts with iron-based materials. The c-BN, another typical superhard material, is difficult to synthesize, which limits its practical application. Therefore, development of novel superhard multifunctional materials is an urgent requirement.

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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 α-Nb₃C was the lowest, which indicated that the formation of α-Nb₃C was feasible. To date, controversy still remains regarding the orthorhombic phase structure of Nb₂C.

In this article, we performed a crystal structure search for the Nb–C system using an 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 Nb₂C at high pressures. The predicted new phase of Nb₂C belongs to the orthorhombic Pnmm 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 sp³ hybridization style, which further knitted into three-dimensional networks. Collectively, we proved that Nb₂C can be a potential candidate for an ultra-stiff and hard material.

3 Results and discussion

In this study, we uncovered a stable structure of Nb₂C, denoted as Nb₁ₓC₁₋ₓ. At first, we calculated the formation enthalpy of NbₓC₁₋ₓ using a fractional representation of NbₓC₁₋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 C concentration, the Nb was constructed, which is plotted in Fig. 3. With the increase in a pressure –

† Wu’s studies. The values, which indicates that Nb$_2$C- is thermodynamically stable under pressure. From Fig. 1(d), it can be observed that at 50 GPa, the stable phases are only NbC and Nb$_6$C$_5$. We calculated the detailed enthalpy differences as a function of pressure. As shown in the ESI Fig. S1(a), 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-Pnma are calculated against decomposition into the constituent carbides. As shown in Fig. S1(b) and (c), the structures of Nb$_6$C$_5$ and Nb$_2$C-Pnma 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 Pnma structure, as we predicted, contains two Nb$_2$C in a unit cell at 20 GPa (a = 5.415 Å, b = 4.837 Å, and c = 3.019 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 Pnma phase. Fig. 4(d) shows the structure of Pnma phase along the y-axis. When we compare Fig. 4(b) with (d), it was observed that the carbon atoms in Nb$_2$C-Pnma 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 NbC have no soft mode in the Brillouin zone, indicating that NbC is dynamically stable. For the purpose of understanding the mechanical properties, the elastic constants are deemed essential. The elastic constants C$_{ij}$ of the Pnma phases are listed in Table 2. For the proposed Nb$_2$C-Pnma, all C$_{ij}$ satisfy Born–Huang criteria, which means that the proposed Nb$_2$C-Pnma is mechanically stable. We determined that the Nb$_2$C-Pnma 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 NbC 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 a-axis. Therefore, there is certain disparity between C$_{33}$ 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-Pnma is 244 and 310 GPa, respectively, which are larger than the values of Nb$_2$C-Pnma (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,

Fig. 2 Enthalpy–pressure diagrams. Calculated enthalpies as the function of pressure.

Fig. 3 Pressure–composition phase diagrams.
the Poisson’s ratio \(r\) of Nb\(_2\)C-\(Pnnm\) is about 0.19. Usually, strong directionality degree of covalent bonding is considered in the materials when the \(r\) value is near 0.2, indicating that the directionality degree of covalent bonding of Nb\(_2\)C-\(Pnnm\) is strong. The Pugh’s indicator \(G/B\) 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.,\(^6\) 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:

\[
H_V = (k^2G)^{0.585} - 3 (k = G/B)
\]

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 \(d\) electrons 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 |
indicates that mixed bonds between the two atoms are present in this area, in which the ionic bonds are dominant. As Becke defined,49 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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