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Predicting New Superhard Phases

The search for new superhard materials is of great importance in view of their major roles played for the fundamental science and the industrial applications. Recent experimental synthesis has made several great successes, but the synthetic difficulty in general remains. Materials design technique is greatly desirable as a request to assist experiment. In this paper, two rational theoretical methods of design of superhard materials have been reviewed: (i) substitutional method, which is successful in some cases, but limited to the known chemically related phases, and (ii) global free energy minimization method, which can be applied to large scale of materials with the only information of chemical compositions. The successful applications have been described and the main principles are summarized.

Key words: *superhard materials, crystal structure prediction, substitutional method, free energy minimization method, first-principles.*

INTRODUCTION

Superhard materials are of great importance in science and technology, with applications in abrasives, coatings, cutting, polishing tools, etc. Hardness, in general, is understood as the extent to which a given solid resists both elastic and plastic deformations [1]. Hard materials usually refer to materials with hardness (here referred to Vickers hardness) greater than 20 GPa, while materials with hardness above 40 GPa are classified as superhard materials [2]. Experimentally, (nano)diamond remains the hardest known substance with the hardness reaching 100–160 GPa, though over the past decades extensive experimental efforts have been devoted to exploring new materials that could be harder than diamond. However, diamond is exceptionally weak for ferrous metals cutting and is burned to carbon dioxide at 800–900 °C in air. These shortcomings have significantly limited its application. Another well-known superhard material is cubic boron nitride (cBN), which has been considered as the second hardest material for a long time. cBN possesses fascinating properties, such as high thermal stability (~1650 K) and low chemical reactivity. However, the hardness of cBN is only in the range of 46–66 GPa, which is evidently much smaller than that of diamond. Therefore, the quest for new superhard materials with the hardness exceeding that of cBN (or even diamond) and better thermal stability than diamond, is highly demanded.

In search for new superhard materials over the past several decades, scientists mainly focused on the exploration of covalent compounds formed by light elements, namely, boron (B), carbon (C), nitrogen (N), and oxygen (O), since these elements have the ability to form short and strong three-dimensional covalent bonds (e.g., sp^3 bonds), which is a necessary condition for superhard materials. The lightest element that could produce three-dimensional structure, beryllium, has been often neglected to synthesize superhard materials, perhaps because it is toxic and may require specialized high-pressure equipment [3]. Following this route,

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great experimental progress is achieved with the successful synthesis of cBC_xN [4–8], B_2CN [9], cBC_5 [10], boron suboxide (e.g., B_6O) [11], γ-B_{28} [12–14], B_4C [15], boron subnitride (e.g., $B_{13}N_2$) [16], and so on. Except for B2CN, they have been experimentally reported as superhard materials. The hardness of diamond-like cBC_2N and cBC_5 even reach 76 (62) and 71 GPa, respectively, which are higher than that of cBN. Very recently, a new family of materials formed by heavy transition metals and light elements are proposed to be potential superhard since heavy transition metals can basically introduce high valence electron density into the compounds to resist both elastic and plastic deformation. Many these compounds have then been successfully synthesized, such as, transition metal nitrides [17–21], carbides [22], and borides [23–28]. These compounds possess ultrahigh bulk moduli (428 GPa for IrN_2[20]) comparable with those of the traditional superhard materials. Though there exists extensive debates [26, 27], ReB_2 and WB_4 have been claimed to be superhard [24, 25, 29].

Earlier experiments indeed have made big progress in synthesizing several new superhard materials, but the well-known synthetic difficult remains. The blind synthesis of superhard materials requires a lot of different tries, such as the choice of precursor materials, synthetic temperature and pressure, etc., which normally need a large amount of manpower and materials resources. However, it is quite often that the synthesis faces little rate of success, as well as low efficiency. One of the causes might stem from the fact that some materials can only be stabilized in a very narrow temperature and pressure regime. Therefore, there is an urgent need for robust methods of designing new superhard materials. Once a promising energetic phase has been predicted and the appropriate synthetic conditions (e.g., external pressure, temperature, and starting materials) could be suggested to help for the experimental synthesis in a more effective way.

Recently, many hardness models are proposed to evaluate the intrinsic hardness of ideal crystals and are quite successful for the applications to covalent compounds, and even for metals [1, 30–40]. These hardness models made possible the theoretical prediction of hardness and are thus greatly helpful for the design of new superhard materials. It is well accepted that the exploration of new crystal forms is central to design of new superhard materials. At the current stage, there are mainly two ways to predict new superhard phases: (i) substitutional method (based on the phases of known materials) and (ii) free energy minimization method (dedicated to predicting the most stable crystal structure from scratch). This paper reviews the present status of predicting new superhard phases limited to the above two methods.

SUBSTITUTIONAL METHOD

Principles and Applications

"Substitutional method" is an easy-to-use method, which depends on the known structural database and follows the criteria that a material with a particular chemical formula (e.g., A_mB_n) has a structural type, which is known in other chemically related materials. This method can be successful if the target crystal forms of materials are already documented in the structural database. The well-known hypothetic superhard material, hexagonal β-C_3N_4 [Fig. 1b], was proposed by Liu and Cohen [41, 42] through this method with the knowledge of known β-Si_3N_4 structure by substituting C for Si. The notion that C–N bond in β-C_3N_4 is shorter than C–C bond in diamond has attracted much attention. It is then remarkably predicted that the bulk modulus of β-C_3N_4 could be higher than that of

diamond [42]. This prediction has motivated extensive experimental exploration [43—51] of carbon nitrides, though the synthesis of this intriguing β-C_3N_4 still remains elusive. Subsequent theoretical calculations further proposed other dense polymorphs of C_3N_4 (Fig. 1), e.g., hexagonal α-C_3N_4, cubic C_3N_4 (cC_3N_4), the cubic phase with defect zinc-blende structure ($dzbC_3N_4$), and the pseudocubic phase (pcC_3N_4), among which cC_3N_4 has a zero-pressure bulk modulus exceeding that of diamond [52, 53]. With the structural information of C_3N_4, several boron carbides, e.g., α-B_4C_3, β-B_4C_3 and pseudocubic B_4C_3 were constructed by replacing N with B atoms [54]. The predicted hardness of these B_4C_3 phases can reach 51–63 GPa. These predictions clearly pointed out the possible existence of potential superhard candidates; however, the experimental synthesis of these promising materials has been intensely debated and it has been clear that much experimental effort is required.
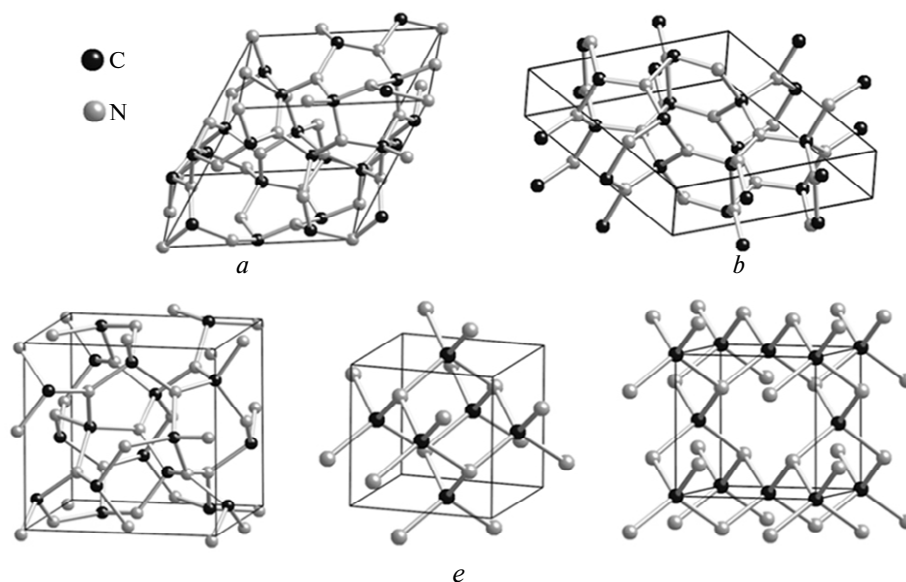

Fig. 1. Crystal structures of α-C_3N_4 (*a*), β-C_3N_4 (*b*), cC_3N_4 (*c*), $dzbC_3N_4$ (*d*), and pcC_3N_4 (*e*) phases.

Considerable efforts have also been devoted to the synthesis and modeling of ternary B–C–N materials. Following the typical expectation that most of the superhard materials are insulators or semiconductors, since the metallic component has negative effect on hardness, different combinations of B, C, and N can be proposed for the search of novel isoelectronic structures with that of diamond, while the following simple rule [55] should be obeyed: $pZ_V(B) + mZ_V(C) + lZ_V(N) = 4n$. The values p, m, l, and n are integers, and $Z_V(B)$, $Z_V(C)$, and $Z_V(N)$ are the atomic valence states (2s and 2p) for B, C, and N, respectively. Classical examples are BN, C_3N_4, $C_{11}N_4$, and BC_xN, etc. Experimentally, several diamond-like BC_xN (x = 1, 2, 3.3, 4, and 6) have been successfully synthesized [4—8]. Diamond-like BC_2N (cBC_2N) has gained extensive attention and the reported hardness is in the range of 62—76 GPa, much higher than that of cBN. However, the crystal structure of the synthesized sample is unknown, precluding the understanding of the superhardness. Many theoretical works are thus performed to explore the crystal structure of cBC_2N, mainly by using the substitutional method.

Many interesting structures are proposed, such as the chalcopyrite structure (cpBC$_2$N) [56], body-centered structure (bcBC$_2$N) [57, 58] based on a hypothetical body-centered sp^3-bonded carbon (Fig. 2, a), three wurtzite-type structures, zBC$_2$N, and tBC$_2$N structures [59, 60] constructed from the sixteen-atom supercell of diamond. However, the true crystal structure of cBC$_2$N still remains debatable.
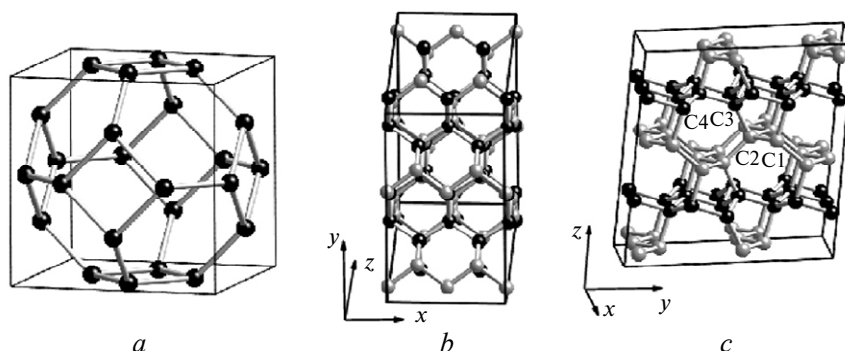

Fig. 2. (a) C$_6$ body-centered cubic structure, (b) and (c) polyhedral views of the crystal structure of M-carbon. The grey and black spheres represent the different warped "layers".

For the compounds formed by heavy transition metals and light elements, a variety of structure types within the substitutional methodology were considered to design new superhard materials, including the zinc-blende, rock salt, pyrite, rutile, fluorite, WC, CaCl$_2$, MoC$_2$, and CoSb$_2$ types [61—72]. The theoretical results demonstrated that these compounds possess ultrahigh bulk modulus (ultra-incompressibility). Interestingly, Gou et al. [70] even predicted that the incompressibility of ReC within hexagonal WC–type structure exceeds that of diamond at the pressure above 30 (49) GPa with local-density approximation (generalized gradient approximation). The theoretical calculations for these heavy transition metals' compounds draw a clear conclusion that the highly directional light element–light element bonds with large electron densities are short and strong; however, the transition metal–light element bonds with lower electron densities are long and weak. This anisotropic bonding behavior might be a severe problem for the hardness. In addition, the bonds in the compound formed by heavy transition metals and light elements typically have metallic component, which is delocalized and might be negatively related to hardness [35, 70]. Thus, design of superhard phases in these compounds requires a particular attention to the nonmetallic materials with isotropic bonding environment.

Limitation

The substitutional method is successful in design of new superhard materials for some particular cases. As we have described above, the proposed structures with X substituted for Y atoms are based on the knowledge of known chemically related structures; however, there is a possibility that hitherto unknown structures are energetically stable instead. Worst of all, it is particularly difficult to explore the stable crystal structure for compounds formed by B, C, N, and O elements. It is known that B, C, N, and O can adopt a wide range of complicated structures because of their ability to form sp-, sp^2-, and sp^3-hybridized bonds. As an illustrative case, for carbon, the flexibility of hybridized bonds results in diverse and unexpected polymorphs, such as hexagonal lH (l = 2, 10, and 12) and rhombohedral 3R graphite, cubic 3C, hexagonal mH (m = 2, 8, 12, 16, and 20) and rhombohedral nR (n = 15 and 21) diamond, M-carbon [73], chaoite, nanotubes,

fullerences and amorphous carbon. Problems inevitably arise in substitutional method when unexpected crystal structures appear (like for carbon) but not in the list of structural database of known materials.

GLOBAL FREE ENERGY MINIMIZATION METHOD

Principles

Based on the fact that the most stable crystal structure has the lowest Gibbs free energy at given p, T conditions, several structural prediction methods, which do not require any prior knowledge or assumptions about the system, such as evolutionary methodology [74—76], simulated annealing [77—79], minima hopping [80], and metadynamics [81], have been developed to predict the stable crystal structures. The evolutionary method for crystal structure prediction [74—76] has been very successful to explore the stable crystal structures with the only known information of chemical compositions [12, 73—76, 82—93]. It is accepted that the energetically most stable phases (or some low-energy metastable phases) of the target materials are more likely to be synthesized under carefully chosen experimental conditions (if possible, at the theoretically suggested pressure and temperature region). Here we present some applications of the evolutionary algorithm of design of superhard materials targeting on the technically important systems, such as the compounds formed by light elements or by heavy transition metals and light elements.

Applications

M-carbon. Under high pressure, carbon and its symmetrical analogs exhibit a tendency to form strong directional bonds, especially when the electronegativity difference between the two bonding atoms is small (e.g., diamond and cBN). We have thus extensively explored the crystal structures of elemental carbon under pressure (0~100 GPa). Remarkably, a novel monoclinic phase (named as *M*-carbon) with $C2/m$ symmetry was uncovered to be stable over graphite above 13.4 GPa as shown in Figs. 2, *b* and *c*. The crystal is made of exclusively three-dimensional sp^3 hybridized covalent bonds, just as in the well-known (2×1) reconstruction of the (111) surface of diamond and silicon. Since *M*-carbon presents six-fold rings forming warped "layers", this intriguing phase can be understood as distorted graphite. Strikingly, this new polymorph of carbon possesses a very high hardness of 83 GPa estimated by Šimůnek's model [1] and bulk modulus of 431 GPa, which are comparable to those of diamond. Experimentally, it is known that graphite can convert to a superhard unknown phase above 14 GPa at room temperature [94–99]. We here proposed that *M*-carbon is a likely candidate for this cold-compressed graphite, since the experimentally observed changes in X-ray diffraction pattern, near K-edge spectroscopy, and electrical resistance of this superhard phase are well explained by the coexistence of *M*-carbon and graphite [73].

cBC₂N. To clarify the intensive debate on the superhard phase of cBC$_2$N [100, 101], we have extensively explored the crystal structure of BC$_2$N using *ab initio* evolutionary methodology. We have predicted three polytypic structural families: orthorhombic *Pmm*2-*n*u, hexagonal *P*3*m*1-*n*u, and rhombohedral *R*3*m*-*n*u [82], as depicted in Fig. 3. Here *n* denotes that the structure contains *n* BC$_2$N units per primitive cell (*n* = 1, 2, 4). Besides, we have reproduced four phases proposed earlier: *Pmm*2-1u is identical to struc-1 [102]; *P*3*m*1-1u is in accordance with the BC$_2$N-*w*3 [58]; the *R*3*m*-1u and *R*3*m*-2u have been proposed as BC$_2$N$_{1×1}$ and

$BC_2N_{2\times2}$ [103], respectively. Analysis of the total energy, simulated X-ray diffraction pattern, and energy-loss near-edge spectroscopy suggests that our predicted $R3m$-2u is the best candidate phase for the observed superhard BC_2N. We have also demonstrated that the previously proposed high density and low density forms might be identical and their X-ray diffraction patterns could be reasonably understood by the single phase of $R3m$-2u (Figs. 4 and 5). The estimated theoretical Vickers hardness [1] of $R3m$-2u BC_2N is 62 GPa, in excellent agreement with the experimental value of 62 GPa by Zhao et al. [7] and slightly lower than the value of 76 ± 4 GPa measured by Solozhenko et al. [5]. It is significant to note that the hardness of $R3m$-2u BC_2N exceeds that of cBN in this calculation, which is consistent with the experimental results [5, 7].
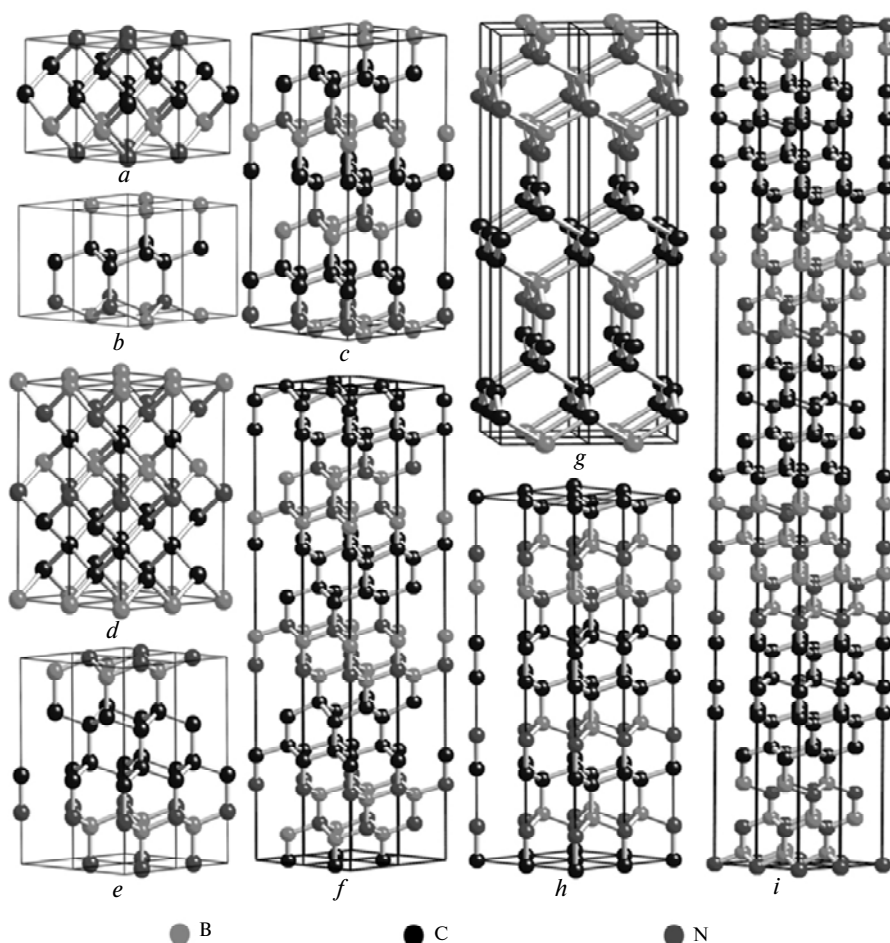

Fig. 3. Crystal structures of c-BC_2N. $Pmm2$-1u (a), $P3m1$-1u (b), $R3m$-1u (c), $Pmm2$-2u (d), $P3m1$-2u (e), $R3m$-2u (f), $Pmm2$-4u (g), $P3m1$-4u (h), and $R3m$-4u (i).

cBC_5. Boron-doped diamond shows higher resistance to oxidation and ferrous metals than diamond and can be expanded to applications to electric devices [104, 105]. Constructing from the supercell of diamond, sandwich-like BC_3, BC_5, and BC_7 structures were proposed and widely studied [35, 106—111]. Recently, diamond-like cBC_5 [10] with a high B content has been successfully synthesized. The obtained cBC_5 sample has been measured to possess a large bulk modulus (335 GPa), unusually high fracture toughness (9.5 MPa m$^{0.5}$), high thermal stability (up to 1900 K), and extremely high hardness (71 GPa). More intriguingly, the

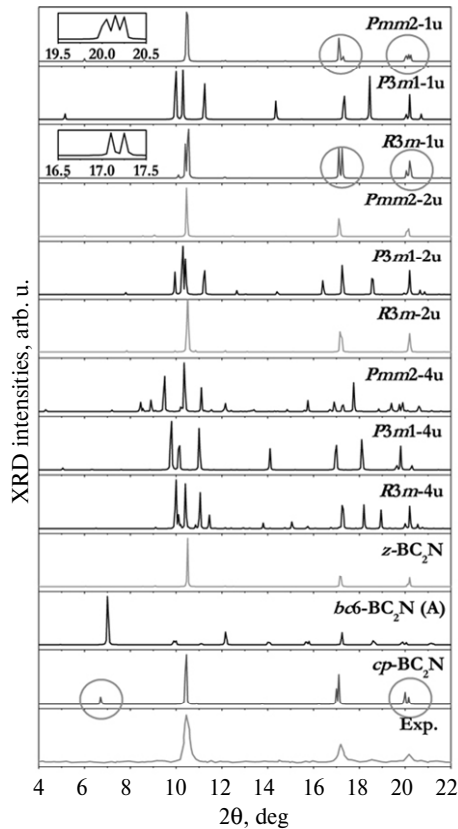Fig. 4. Simulated X-ray diffraction (XRD) patterns of the currently obtained and earlier proposed structure with $\lambda = 0.3738$ Å. The experimental XRD spectrum from Ref. [5] is also shown for comparison.

synthesized BC_5 has been suggested to be superconducting with $T_c = 45$ K [107]. Thus, cBC_5 may be expected as an excellent example to combine the high hardness, high chemical stability, and superconductivity, which are of considerable interest for the creation of high-pressure devices for investigating electric and superconducting properties of various materials under pressure. In order to identify the experimentally synthesized phase and uncover other new superhard phases, we investigated BC_5 over a wide pressure range of 0 to 100 GPa using the evolutionary algorithm [112]. Several intriguing low-energy phases all possessing sp^3 hybridizations were uncovered (Fig. 6). After examining the dynamical stability, the energetically most preferable polymorphs are two orthorhombic Pmma phases (*Pmma*-1 and *Pmma*-2). The simulated X-ray diffraction patterns, Raman modes of the two *Pmma* phases show remarkable agreement with the experimental data [10]. On the basis of microscopic hardness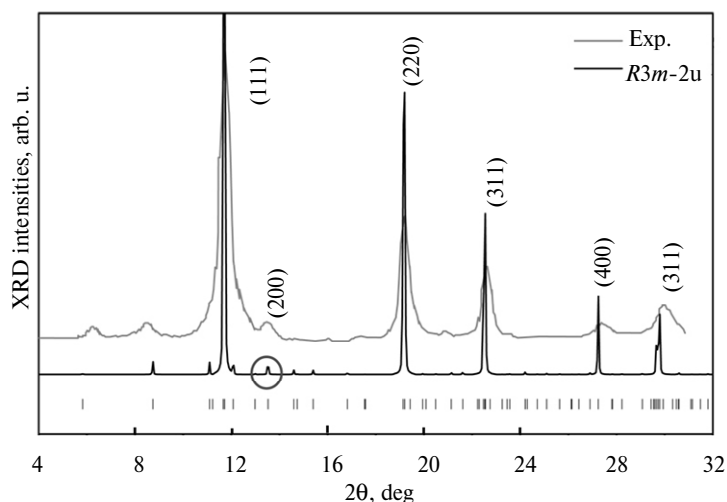 model [30, 31], the Vickers hardness of the two *Pmma* structures have been estimated to be 74 and 70 GPa, respectively, in satisfactory agreement with the experimental data (71 GPa). In previous studies [35, 70], it was found that metallic component has a negative effect on hardness and thus, the correction of metallic bonding is necessary to account for the experimental hardness of electron conductors. The underlying mechanism is that the electrons delocalized to contribute to the conduction should be excluded from the hardness calculation. However, for hole conductors, such as cBC_5, the major carriers are holes and the valence electrons are mainly localized to form covalent bonds. It is thus unnecessary to include the metallic correction in the hardness calculation for cBC_5.

Be₃N₂. Be_3N_2 is one of symmetrical isoelectronic analogs to diamond. It has two known polymorphs: a defect anti-fluorite α-Be_3N_2 with widely direct band gaps has attracted considerable interests for the optoelectronic light-emitting devices and a hexagonal β-Be_3N_2 with good covalence property has been predicted as potentially hard material [113, 114]. Based on the known cubic Mg_3P_2-type structure, Gou et al. [115] predicted a superhard semiconducting phase of Be_3N_2 (γ-Be_3N_2). The calculated hardness value of γ-Be_3N_2 is 51.5 GPa, which approaches those of B_4C and B_6O. This inevitably stimulates further exploration of other unexpected forms of Be_3N_2. Our evolutionary simulations [116] uncovered two novel polymorphs: $R3m$ (3 units/cell) and P-$3m1$ (1 unit/cell), as shown in Fig. 7.

Fig. 5. Comparison of simulated and experimental (Ref. [7]) XRD patterns with λ = 0.4246 Å.
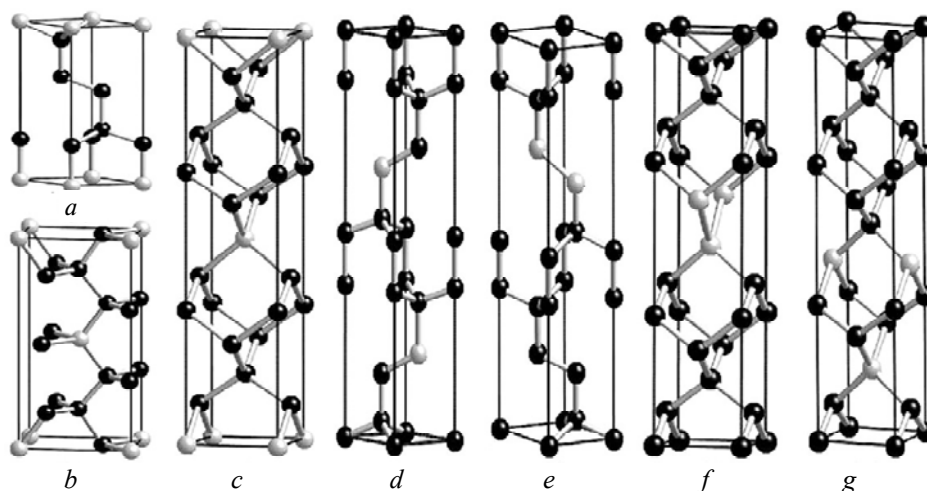
Fig. 6. Crystal structures of cBC5. *P3m*1 (*a*), *Imm*2 (*b*), *I*-4*m*2 (*c*), *P*-3*m*1-1 (*d*), *P*-3*m*1-2 (*e*), *Pmma*-1 (*f*), and *Pmma*-2 (*g*). The B and C atoms are represented as gray and black spheres, respectively.

The calculated enthalpy difference indicates that the *R*3*m* phase is a metastable phase, but it is much more stable (1.180 eV/f.u.) than earlier proposed γ-Be₃N₂. The predicted *P*-3*m*1 phase becomes energetically preferable to β-phase above 76 GPa and becomes most stable above 118 GPa among all the phases. Remarkably, the calculated polycrystalline hardness by using Gao's method [32] is 51 GPa for *R*3*m* and 54 GPa for *P*-3*m*1, which are greater than 40 GPa. Note that the two crystalline phases of Be_3N_2 uncovered here do not have the lowest energy at low pressure region; however, it does not preclude the possibility of their synthesis in the laboratory. For example, β-Be_3N_2 is a metastable phase with a higher energy of 0.148 eV/f.u. compared to α-Be_3N_2, but it has been synthesized by heating the α-Be_3N_2 up to 1640 K. For the predicted *R*3*m* phase, the total energy is 0.25 eV/f.u. higher than for α-Be_3N_2 and hence, the synthesis of this phase can be expected at a higher temperature of about 2000—3000 K.

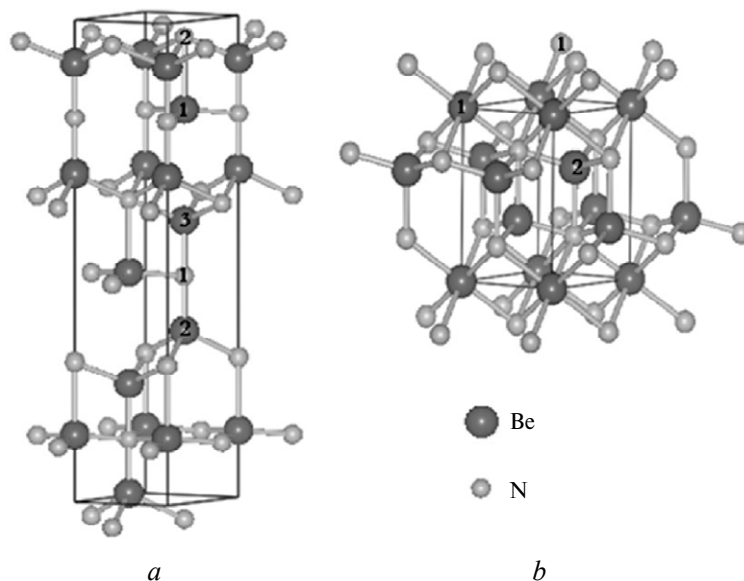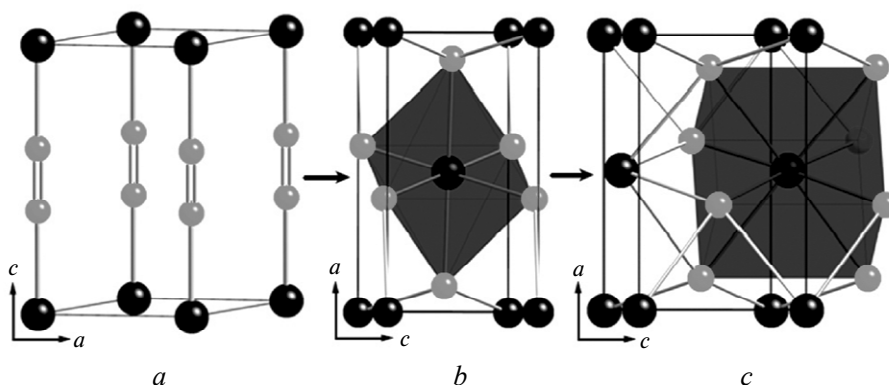Fig. 7. Polyhedral views of $R3m$ (*a*) and P-$3m1$ (*b*) phases for Be_3N_2.

Fig. 8. Crystal structures of the MN_2. $P6/mmm$ (*a*), marcasite (*b*), and $P4/mbm$ (*c*). The M and N atoms are represented as large and small spheres, respectively.

MN_2 *(M = Os, Ir, Ru, Rh)*. We have extensively explored the potential superhard phases for four MN_2 (M = Os, Ir, Ru, and Rh) compounds by using evolutionary methodology. A hexagonal $P6/mmm$ phase (Fig. 8, *a*) is unraveled to be the universal ground state phase for these compounds at low pressures [90], which is energetically much superior to the earlier phases. In this phase, the diatomic N_2 unit is for the first time found to possess double–bonded N=N character in the transition metal nitrides. The $P6/mmm$ phase has short and strong covalent M–N and N=N bonds, resulting in an unusual high incompressibility along the *c* axis. The $P6/mmm$ phase is synthesizable at rather low and readily attainable pressures (~ 40 GPa). In addition, another new tetragonal $P4/mbm$ phase (Fig. 8, *c*) is found to be stable at higher pressures for all these nitrides and can be obtained through the phase transformation via the marcasite phase (Fig. 8, *b*). The predicted unified phase diagram of $P6/mmm \rightarrow$ marcasite $\rightarrow P4/mbm$ upon compression is of fundamental interest in view of the distinct chemistry changes. The transition follows the elevated two, six, and eight coordination numbers.

Interestingly, we found an extremely large C_{33} value in the *P6/mmm* phases for all nitrides, reflecting the high incompressibility along the *c* axis (e.g., 1403 GPa for OsN$_2$). The large C_{33} could be well understood by the strong covalent Os–N and N=N bonds along the *c* axis. Since *P6/mmm* phase possesses only one dimensional bond and the hardness is not expected to be large. The electronic properties calculations reveal clear electron conductor characters for all the above compounds. The hardness calculations rule out the possibility of marcasite phases as superhard materials (e.g., 27 GPa for OsN$_2$), using the microscopic model by taking into account the effects of metallicity [35]. The delocalized electrons contribute to the conduction rather than form covalent bonds, which are responsible for the low hardness.

WN$_2$. In an attempt to design superhard phases within the compounds formed by heavy transition metals and light elements, we also explored the phase diagram of WN$_2$. We have found two ultra-incompressible hexagonal phases of *P6$_3$/mmc* and *P-6m*2 (Fig. 9), which are energetically much superior to previously proposed baddeleyite– and cotunnite–type phases and stable against decomposition into a mixture of W+N$_2$ or WN+1/2N$_2$ [85]. These two new phases do not have analogues in other compounds, however, the *P6$_3$/mmc* and *P-6m*2 structures can be viewed as NiAs–type and WC–type structures with dinitrogen occupying the Ni and C positions, respectively. The calculated large bulk modulus (~ 411 GPa) for the two phases reveals that they are ultra-incompressible materials. The ultra-incompressibility is attributed to a staking of N–W–N "sandwiches" layers linked by strong covalent N–N single bonding. Remarkably, the calculated polycrystalline shear modulus are also very large, 252 GPa for *P6$_3$/mmc* and 255 GPa for *P-6m*2. Thermodynamic study suggests that these phases are synthesizable at above 30 GPa. The estimated theoretical Vickers hardness [1] for the *P6$_3$/mmc* and *P-6m*2 phases are both 37 GPa, which beyond the hardness values of α-SiO$_2$ (30.6 GPa) and β-Si$_3$N$_4$ (30.3 GPa). We attribute the excellent mechanical properties of the two phases to the stacking of N–W–N sandwiches layers linked through strong covalent N–N single bonds. We wish that the above predicted (super)hard phases will stimulate extensive experimental synthesis of these technologically important materials.
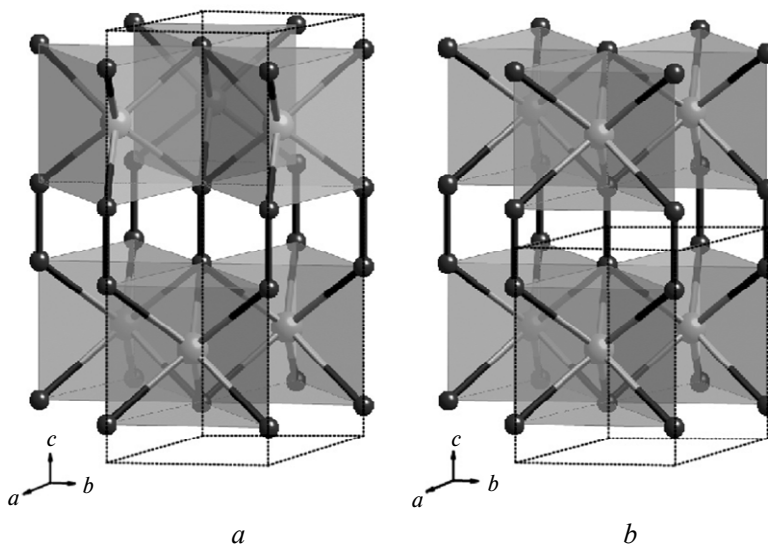

Fig. 9. Polyhedral views of the *P6$_3$/mmc* (*a*) and *P-6m*2 (*b*) structures for WN$_2$. The large and small spheres represent W and N atoms, respectively.

CONCLUSIONS

This paper reviews the present advancement in design of new superhard materials. Substitutional and free energy minimization methods are two frequently adopted methodologies to predict superhard phases and to help in the identification of superhard phases synthesized experimentally, where limited experimental information is known and unable to uncover the crystal structures. Free energy minimization method (here, evolutionary algorithm) has a great advantage in a fact that it is basically unbiased by any known information and relies only on the chemical compositions. The densely packed, three-dimensional and strongly covalent bonded compounds formed by light elements are the preferred targets in search for new superhard phases. To obtain novel superhard materials with conductivity for electric applications, one might have to focus on hole conductors as suggested by the study on BC_5. At the current stage, it still remains a challenge to obtain superhard materials within the compounds formed by heavy transition metals and light elements. The possible solutions might be the search for nonmetallic specimen or pay particular attention to the materials, which are isotropically bonded. With the increasing demand for high performance superhard materials, the scientific challenge of finding superhard phases that surpass diamond will keep the great interest for years and numerous researches are required. Theoretical design of superhard materials will inevitably play a significant role to fulfill the task.

Пошуки нових надтвердих матеріалів дуже важливі як з погляду їх ролі для фундаментальної науки, так і промислового застосування. Нещодавно було проведено декілька дуже успішних експериментів синтезу, однак труднощі синтезу загалом збереглися. Для допомоги в експериментах дуже потрібна техніка проектування матеріалів. У даній статті розглянуто два раціональні теоретичні методи дизайну надтвердих матеріалів: (1) метод заміщення, який є успішним у деяких випадках, але обмежується відомими хімічно спорідненими фазами, і (2) метод глобальної мінімізації вільної енергії, який може бути застосований до великої кількості матеріалів при наявності тільки інформації про хімічний склад.

Ключові слова: надтверді матеріали, прогнозування кристалічної структури, метод заміщення, метод мінімізації вільної енергії, перші принципи.

Поиски новых сверхтвердых материалов очень важны как с точки зрения их роли для фундаментальной науки, так и промышленного применения. Недавно было проведено несколько очень успешных экспериментов синтеза, однако трудности синтеза в общем сохранились. Для помощи в экспериментах нужна техника проектирования материалов. В данной статье рассмотрены два рациональных теоретических метода дизайна сверхтвердых материалов: (1) метод замещения, который является успешным в некоторых случаях, но ограничивается известными химически родственными фазами, и (2) метод глобальной минимизации свободной энергии, который может быть применен к большому количеству материалов при наличии только информации о химических составах.

Ключевые слова: сверхтвердые материалы, прогнозирование кристаллической структуры, метод замещения, метод минимизации свободной энергии, первые принципы.

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