Elastic Properties and Stacking Fault Energies of Borides, Carbides and Nitrides from First-Principles Calculations

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Abstract

Owing to the excellent elastic properties and chemical stability, binary metal or light element borides, carbides and nitrides have been extensively applied as hard and low-compressible materials. Researchers are searching for harder materials all the time. Recently, the successful fabrication of nano-twinned cubic BN (Tian et al. Nature 493:385–388, 2013) and diamond (Huang et al. Nature 510:250–253, 2014) exhibiting superior properties than their twin-free counterparts allows an efficient way to be harder. From this point of view, the borides, carbides and nitrides may be stronger by introducing twins, whose formation tendency can be measured using stacking fault energies (SFEs). The lower the SFEs, the easier the formation of twins. In the present study, by means of first-principles calculations, we first calculated the fundamental elastic constants of forty-two borides, seventeen carbides and thirty-one nitrides, and their moduli, elastic anisotropy factors and bonding characters were accordingly derived. Then, the SFEs of the $\{111\} \langle 112 \rangle$ glide system of twenty-seven compounds with the space group $F\bar{4}3m$ or $Fm\bar{3}m$ were calculated. Based on the obtained elastic properties and SFEs, we find that (1) light element compounds usually exhibit superior elastic properties over the metal borides, carbides or nitrides; (2) the *5d* transition-metal compounds (ReB₂, WB, OsC, RuC, WC, OsN₂, TaN and WN) possess comparable bulk modulus (*B*) with that of cBN (*B* = 363 GPa); (3) twins may form in ZrB, HfN, PtN, VN and ZrN, since their SFEs are lower or slightly higher than that of diamond (SFE = 277 mJ/m²). Our work can be used as a valuable database to compare these compounds.

Keywords Inorganic compounds · Elastic properties · Stacking fault energies · First-principles calculations

1 Introduction

Due to the combination of electron-rich transition-metal (TM) atoms and strong covalent-bonded atoms (e.g., B, C and N), most of the binary TM borides, carbides and nitrides are mechanically hard and incompressible materials [1–3]. They show relative high modulus, ultra-high melting point

and good chemical stability. Hence, they are widely used or have potential in cutting, wear- and corrosion-resistant coating fields [1, 4–6]. For instance, chromium nitride and titanium nitride coatings can enhance the performance of cutting tools [5, 7]. As reinforcements, TiB whiskers or SiC fibers could be added into alloys or ceramics to fabricate composite materials [8–11]. They also might serve as functional materials. For example, magnesium diboride has been proved to be a superconductor [12]. Nickel and cobalt borides are known for their magnetic properties and could be used as catalyst for hydrogen production [13].

Researchers have never stopped searching for super-hard and ultra-incompressible materials. Many experiments and ab initio calculations have conducted, and these works mainly focus on the combination of *3d–5d* TMs with light elements (B, C and N) or the light elements with themselves [14–21]. The experimental synthesized PtN [15] and PtN₂ [16] and the first-principles calculation-predicted Re₄C [18] have comparable bulk moduli with cBN (~ 379 GPa). Nano-twinned cBN [22] and diamond [23], which are

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much harder than their twin-free counterparts, have been successfully fabricated from onion-like precursors at high temperature and high pressure. Twinning can also induce elastic strengthening in SiC nano-wires [24]. Recently, the SFEs and twinnability have been theoretically studied for the group IV TM carbides [25, 26]. The twin boundaries can serve as barriers for dislocation motion or be regarded as grain boundaries, which can decrease the grain size. The Hall–Petch relationship σ is proportional to $d^{-1/2}$ (σ denotes yield strength or hardness and d is the grain size) [27, 28], showing that the smaller the grain size, the stronger (the harder) the material. Previous reported twinned cBN, diamond and SiC possess excellent elastic properties; therefore, twinning is helpful for improving the hardness. The tendency for twin formation can be measured by stacking fault energies (SFEs, γ), which is an intrinsic parameter for one material at finite temperature. More twins are found in alloys with lower SFEs [29–31]. For instance, twins are frequently detected in Cu-16 at.% Al ($\gamma \sim 6$ mJ/m²) than Cu-2.3 at.% Al ($\gamma \sim 48$ mJ/m²) [30]. Meanwhile, twins are quite common in silver ($\gamma \sim 18$ mJ/m²), while they are rarely seen in coarse grain aluminum ($\gamma \sim 130$ mJ/m²) [32]. Therefore, SFEs are important parameters for determining the twinning ability of borides, carbides and nitrides.

The mechanical properties of the material are closely related to the crystal structure, atomic composition, bonding and defects (e.g., twins). In this study, the elastic constants of ninety binary borides, carbides and nitrides will be carried out by employing first-principles calculations. The elastic anisotropy factors and bonding characters will be discussed. Supercells of twenty-seven compounds will also be built to model the SFEs. The materials with SFEs lower than that of diamond (277 mJ/m² in this study) may experience twin formation at the conditions of specific precursor, high temperature, high pressure or high strain rate. The calculated results enrich the understandings of hard and low-compressible materials.

2 Calculation Methods and Models

The elastic properties and SFEs are calculated by employing the Vienna ab initio simulation package (VASP) [33, 34], which is based on the density functional theory (DFT). The projector augmented wave (PAW) method [35] is used to treat the interaction between ion and core electrons. The valence electrons are described using the generalized gradient approximation (GGA) with the exchange–correlation function of Perdew, Burke and Ernzerhof (PBE) [36]. Convergence tests indicate that 600 eV is an appropriate cutoff energy for the PAW potential to obtain fine precision in the current light-elements-contained systems, especially for elastic constants calculations. Brillouin-zone gridding

is performed using the Monkhorst–Pack method [37]. Regarding that the lattice constants (LCs) of the ninety materials are diverse, all of the k-point meshes are carefully tested and tuned. Previous studies show that the non-magnetic P6/mmm-AuB₂ [17], Fm $\bar{3}$ m-ReC [18] and Fm $\bar{3}$ m-CrN [38] are elastically unstable; thus, spin polarization is considered for Au, Re and Cr as well as for Fe, Co and Ni based compounds. Using the optimized input parameters, the calculated energy change converges to smaller than 0.2 meV/atom and the elastic constants C_{ij} change converges to < 5 GPa.

After full relaxation of the cell shape and atom positions, we employ the so-called universal linear-independent coupling strains (ULICs) method proposed by Yu et al. [39] for the elastic properties calculations. For a cubic crystal, there are three independent elastic constants (C_{11} , C_{44} and C_{12}), while an orthogonal (lowest symmetry in the present study) crystal has six more independent elastic constants, i.e., C_{22} , C_{33} , C_{55} , C_{66} , C_{13} and C_{23} . The rhombohedral crystal has C_{14} , C_{15} and C_{45} , but they are extremely small and their contributions to the elastic properties can be ignored. Based on the Voigt approximation [40], five crucial elastic properties, bulk modulus (B), shear modulus (G), Young's modulus (E), Poisson's ratio (ν) and anisotropy factor (A) [41], can be derived from the elastic constants:

$$B = (C_{11} + C_{22} + C_{33})/9 + 2(C_{12} + C_{13} + C_{23})/9, \quad (1)$$

$$G = (C_{11} + C_{22} + C_{33} - C_{12} - C_{13} - C_{23})/15 + (C_{44} + C_{55} + C_{66})/5, \quad (2)$$

$$E = \frac{9BG}{3B + 2G}, \quad (3)$$

$$\nu = \frac{3B - 2G}{6B + 2G}, \quad (4)$$

$$A = C_{66}(C_{11} + 2C_{12} + C_{22}) / (C_{11}C_{12} - C_{12}^2) \quad \text{for the (001) symmetry plane of an orthogonal crystal,} \quad (5)$$

$$A = 2C_{66} / (C_{11} - C_{12}) \quad \text{for the (001) symmetry plane of a tetragonal crystal,} \quad (6)$$

$$A = C_{33}/C_{11} \quad \text{for planes containing the [001] axis of a hexagonal crystal,} \quad (7)$$

$$A = (2C_{44} + C_{12})/C_{11} \quad \text{for the {001} symmetry plane of a cubic crystal,} \quad (8)$$

where B represents the ability to resist fracture, while the reciprocal of B demonstrates compressibility; G represents

the ability to resist plastic deformation. $A = 1$ means a completely isotropy material, while A larger or smaller than unity indicates the degree of elastic anisotropy [42].

The perfectly close-packed stacking sequence of an $F\bar{4}3m$ or $Fm\bar{3}m$ crystal can be expressed as $\cdots A\alpha B\beta C\gamma A\alpha B\beta C\gamma A\cdots$. The crystal structure with a space group (SG) of $F\bar{4}3m$ has two stacking fault sequences $\cdots A\alpha B\beta C\alpha B\beta C\gamma A\cdots$ (denotes as SF1) and $\cdots A\alpha B\beta C\gamma B\beta C\gamma A\cdots$ (SF2) for the $\{111\} \langle 112 \rangle$ glide system. Similarly, the crystal with SG of $Fm\bar{3}m$ also has SF1 ($\cdots A\alpha B\beta B\alpha B\beta C\gamma A\cdots$) and SF2 ($\cdots A\alpha B\beta C\beta B\beta C\gamma A\cdots$) for the $\{111\} \langle 112 \rangle$ glide system, as shown in Fig. 1. A supercell was built with five layers and four atoms in each layer; here, $A\alpha$ or $B\beta$ or $C\gamma$ is regarded as one layer. For calculating the SFEs, an SF lying in the middle of $[111]$ direction is employed. To evaluate the influence between two adjacent SFs along the $[111]$ direction, larger supercells with seven to eleven layers were tested. Tests show that five layers' supercell was large enough to eliminate the interactions with the nearest SFs. Thus, the five layers' supercell is employed for the SFEs calculations. The SFE γ is defined as [43, 44]:

$$\gamma = (E_{sf} - E_p)/S, \quad (9)$$

where S is the cross area of SF, E_{sf} is the energy of a supercell containing one SF, and E_p is the energy of a perfect supercell which has the same atoms as the faulted supercell.

3 Results and Discussion

3.1 Elastic Properties

The elastic properties can be estimated by nano-indentation, tensile testing, ultrasonic measurements or other

experimental methods. However, the experimental values of elastic properties are sensitive to sample preparation, anisotropy and testing methods. Ab initio calculations have been widely used in the determination of elastic properties of the group IV–VI TM (Ti, V, Cr, W, etc.) borides (carbides and nitrides) and show decent agreement with experiments [3, 45, 46]. Here, the calculated lattice constants (LCs) and elastic properties are listed in Tables 1, 2 and 3 for the forty-two borides, seventeen carbides and thirty-one nitrides, respectively. Generally, many elastic-related properties, including moduli, anisotropy factors, bonding characters and Debye temperature [47], can be obtained using the elastic constants. Our calculated results are comparable with the results from the literature (see details in Tables 1, 2, 3). Slight varieties which mainly arise from the input parameters during calculation still exist. For instance, the elastic constants of unrelaxed crystal are different from that of relaxed one [48]; the local density approximation (LDA) pseudopotential usually results in a larger elastic constants than GGA [20, 42, 46]. It should be noted that, during the calculations of elastic constants, the GGA pseudopotential is chosen and the lattice parameters are fully relaxed.

The elastic stability criteria that concern independent elastic constants for a cubic crystal should satisfy $C_{11} > 0$, $C_{44} > 0$, $C_{11} > C_{12}$, $(C_{11} + 2C_{12}) > 0$; for a hexagonal one $C_{11} > C_{12}$, $C_{12} > 0$, $C_{33} > 0$, $C_{44} > 0$, $(C_{11} + C_{12})C_{33} - 2C_{13}^2 > 0$; for a tetragonal crystal $C_{11} > 0$, $C_{33} > 0$, $C_{44} > 0$, $C_{66} > 0$, $C_{11} > C_{12}$, $C_{11} + C_{33} > 2C_{13}$, $(2C_{11} + C_{33} + 2C_{12} + 4C_{13}) > 0$; and for an orthorhombic $C_{11} > 0$, $C_{22} > 0$, $C_{33} > 0$, $C_{44} > 0$, $C_{55} > 0$, $C_{66} > 0$, $C_{11} + C_{22} > 2C_{12}$, $C_{11} + C_{33} > 2C_{13}$, $C_{22} + C_{33} > 2C_{23}$, $(C_{11} + C_{22} + C_{33} + 2C_{12} + 2C_{13} + 2C_{23}) > 0$ [42]. The elastic instability is corresponding to the energetic instability [17]. Based on the above criteria, among the ninety phases, the $P6/mmm$ - AuB_2 [17], $Fm\bar{3}m$ - ReC [18] and

Fig. 1 Illustration of SF structure for SG $F\bar{4}3m$ **a, b, c** and $Fm\bar{3}m$ **d, e, f**. Horizontal direction $[11\bar{2}]$, vertical direction $[111]$, all viewed from $[1\bar{1}0]$. **a, d** Perfect supercells, **b, e** SF1, **c, f** SF2. Red dash line

denotes the SF. Gray and blue spheres represent metal atom and N (or C) atoms, respectively

Table 1 LCs (in Å) and elastic properties (C_{ij} , B , G and E in GPa) of borides at zero pressure

	SG	LCs	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}	B	G	E	ν	A
B	R $\bar{3}m$	5.050	565		505	195		224	117	32		222	220	495	0.128	0.893
AlB ₂	P6/mmm	3.009, 3.285	557		387	47		229	98	5		191, 197 ^a , 191 ^b	158, 132 ^a , 95 ^b	371	0.176	0.696
AuB ₂	P6/mmm	3.011, 4.245	207		127	-23		-30	267	87						
Co ₂ B	I4/mcm	4.955, 4.259	427		335	103		116	199	173		253	107	282	0.314	1.019
CoB	P6mm	3.925, 5.161, 3.065	514	421	484.4	159.9	201.4	147.1	217.7	216.6	223.7	304	152	392	0.285	1.193
Cr ₂ B	I4/mcm	5.127, 4.269	518		485	205		198	172	197		295	185	459	0.241	1.145
CrB	Cmcm	2.925, 7.841, 2.915	505	613	592	222	267	215	186	175	149	303	221	533	0.207	1.166
CrB ₂	P6/mmm	2.960, 3.031	550		423	158		209	133	97		242, 300 ^a , 239 ^b	185, 171 ^a , 140 ^b	442	0.195	0.769
Fe ₂ B	I4/mcm	5.053, 4.232	410		376	144		153	149	126		222	142	350	0.237	1.169
FeB	Pnma	5.410, 2.948, 3.995	388	450	503	208	117	193	240	191	205	290	151	385	0.279	2.179
HfB	Fm $\bar{3}m$	4.835	409			55			67			181	101	256	0.264	0.432
HfB ₂	P6/mmm	3.143, 3.489	605		465	263		269	67	138		262, 270 ^a , 261 ^b	248, 240 ^a , 233 ^b	566	0.141	0.769
MgB ₂	P6/mmm	3.073, 3.515	433		272	72		189	55	32		153, 157 ^a , 152 ^b	134, 132 ^a , 116 ^b	312	0.160	0.628
Mn ₂ B	I4/mcm	5.059, 4.100	534		495	218		163	223	221		321	180	454	0.264	1.052
MnB	Pnma	5.446, 2.983, 4.119	402	518	495	213	164	214	175	151	140	261	181	442	0.218	1.530
MnB ₂	P6/mmm	2.936, 2.986	613		388	129		227	159	125		271, 220 ^b	177, 122 ^b	437	0.231	0.632
Mo ₂ B	I4/mcm	5.545, 4.756	500		463	155		162	189	215		300	150	386	0.285	1.040
MoB	I4 ₁ /amd	3.126, 16.990	560		533	213		241	196	204		318	203	503	0.236	1.325
MoB ₂	P6/mmm	3.030, 3.331	610		431	145		236	137	223		313, 311 ^a , 303 ^b	177, 192 ^a , 186 ^b	446	0.263	0.708
NbB	Cmcm	3.315, 8.784, 3.180	479	532	519	189	234	207	135	165	118	263	200	478	0.197	1.119
NbB ₂	P6/mmm	3.120, 3.338	581		417	207		234	114	196		288, 299 ^a , 286 ^b	201, 220 ^a , 210 ^b	489	0.217	0.716
Ni ₂ B	I4/mcm	4.981, 4.269	404		353	85		131	199	169		248	102	268	0.320	1.279
NiB	Cmcm	2.953, 7.370, 2.986	325	484	405	104	108	120	193	193	160	256	111	291	0.311	1.198
OsB ₂	Pmmn	4.705, 2.889, 4.094	566	552	743	73	184	190	178	172	121	311	182	457	0.255	0.999
Pd ₂ B	Pnmm	4.764, 5.150, 3.156	218	229	244	55	39	91	175	128	138	175	54	146	0.361	3.718
PtB	P6 ₃ /mmc	3.766, 3.647	330		301	47		58	214	247		264	47	134	0.416	0.912
ReB ₂	P6 ₃ /mmc	2.914, 7.505	643		1024	260		244	154	127		348, 355 ^c	280, 289 ^c	661	0.183	1.592
RuB ₂	Pmmn	4.667, 2.882, 4.061	518	460	678	101	210	171	189	142	122	285	176	439	0.243	1.145
Ta ₂ B	I4/mcm	5.794, 4.879	506		429	185		184	104	165		256	178	433	0.218	0.915
TaB	Cmcm	3.294, 8.703, 3.163	525	594	553	204	261	232	156	198	140	296	218	525	0.204	1.155
TaB ₂	P6/mmm	3.099, 3.326	598		450	214		227	144	221		313, 341 ^a , 296 ^b	202, 244 ^a , 192 ^b	498	0.235	0.752
TiB	Pnma	6.114, 3.050, 4.561	425	532	417	194	174	218	96	120	62	214, 207 ^d	190, 186 ^d	441	0.157	1.155
TiB ₂	P6/mmm	3.034, 3.225	653		463	256		292	70	116		264, 261 ^a , 250 ^b	258, 271 ^a , 261 ^b	584	0.130	0.708
VB	Cmcm	3.041, 8.023, 2.965	510	665	616	211	275	208	129	157	70	278	235	549	0.171	0.925
VB ₂	P6/mmm	2.997, 3.025	684		487	221		284	117	138		293, 284 ^a , 280 ^b	243, 247 ^a , 241 ^b	571	0.176	0.711
W ₂ B	I4/mcm	5.572, 4.770	563		528	154		176	211	243		338	161	416	0.295	0.998
WB	I4 ₁ /amd	3.143, 16.924	569		551	227		252	230	249		350	205	515	0.254	1.483

Table 1 (continued)

	SG	LCs	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}	B	G	E	ν	A
WB ₂	P6/mmm	3.018, 3.364	623		421	132		234	154	254		332, 330 ^a , 323 ^b	166, 172 ^a , 164 ^b	428	0.285	0.675
YB ₂	P6/mmm	3.299, 3.867	364		337	158		158	49	79		164, 157 ^a , 171 ^b	152, 150 ^a , 145 ^b	348	0.146	0.927
YB ₆	Pm $\bar{3}$ m	4.102	451			30			30			170	102	256	0.250	0.201
ZrB	Fm $\bar{3}$ m	4.918	369			55			66			167	94	237	0.264	0.478
ZrB ₂	P6/mmm	3.175, 3.558	563		441	250		252	59	136		247, 229 ^a , 239 ^b	233, 231 ^a , 231 ^b	532	0.142	0.783

SG is the abbreviation of space group

^aRef. [17], DFT with GGA^bRef. [19], DFT with GGA^cRef. [20], DFT with GGA^dRef. [48], DFT with GGA

Fm $\bar{3}$ m-MoN with $C_{44} < 0$ and F $\bar{4}$ 3m-PtN with $C_{11} < C_{12}$ [49] are elastically unstable. Besides, Zhou et al. [38] suggest the non-magnetic state Fm $\bar{3}$ m-CrN should also be elastically unstable because C_{44} is quite small (~ 6 GPa), and the spin polarization should be considered.

There are mainly three types of metal borides: M₂B (tetragonal), MB (orthogonal) and MB₂ (hexagonal). Much theoretical attention has been paid on the MB₂ type but not the former two [17, 19, 50]. Here, some interesting conclusions could be drawn by comparing the elastic properties of the three phases from the data listed in Table 1. Generally, the bulk modulus B and shear modulus E of MB₂ are larger than that of MB for group IV and V TM, while it is opposite for group VI TM. Most of the group IV–VII TM borides all exhibit higher elastic properties than boron. At the same time, the values of B for borides within one group are similar. The $5d$ TM borides possess pronounced elastic properties among the forty-two borides. From group IV to VI, the anisotropy character decreases for the $3d$ TM borides while increases for the $4d$ and $5d$ phases. But no special trends of B , G and E are found for $3d$, $4d$ or $5d$ TM borides. These regularities of the borides can be explained by the crystal structures, bonding characters and electronic configurations [3, 50]. Among these borides, ReB₂ and WB give the largest $B \sim 350$ GPa which is comparable with that of cBN (363 GPa). However, the experimental B of ReB₂ is only 173 GPa [51], probably due to the strong anisotropy ($A = 1.59$) or the as-fabricated ReB₂ is not fully dense. All the A values of seven orthogonal MB (except for FeB and MnB) as well as eight tetragonal M₂B are slightly lower or higher than unity which indicates weak anisotropy for the (001) symmetry plane of these phases. Except for ReB₂, the hexagonal borides usually exhibit favorable elastic properties and unobvious anisotropy ($A > 0.63$), while cubic ones have poor elastic properties and strong anisotropy ($A < 0.48$).

The LCs ratio c/a is an important parameter for hexagonal crystals. The B , G and E of thirteen MB₂-type (SG P6/mmm, AuB₂ is excluded for elastic instability) borides against c/a is plotted in Fig. 2. It shows that the three moduli decrease generally as the c/a ratio increases. This trend is attributed to the stronger bonding force and shorter bond length with the smaller c/a ratio. However, the electrons of one metal participating in bonding should also be considered for the scatter of the moduli. In cases, due to the lacking of bonding d -electrons, AlB₂ and MgB₂ exhibit ordinary moduli compared with TM borides; tungsten has one more s -electron than chromium which causes stronger bonding with p -electrons of boron and thus $B(\text{CrB}_2) < B(\text{WB}_2)$ although c/a increases. What's more, besides CrB₂, the difference of B or G is usually found less than 25 GPa within one group (e.g., Ti, Zr, Hf) for TM diborides.

Table 2 LCs (in Å) and elastic properties (C_{ij} , B , G and E in GPa) of carbides at zero pressure

	SG	LCs	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}	B	G	E	ν	A
Diamond	F $\bar{4}3m$	3.572	1029			540			106			414, 433 ^a	509, 534 ^a	1083	0.064	1.153
CrC	Fm $\bar{3}m$	4.069, 4.068 ^b	624			127			194			337, 318 ^b	162, 156 ^b	419	0.293	0.717
		4.107 [*]	461 [*]			80 [*]			121 [*]			234	116	298	0.287	0.608
Cr ₃ C ₂	Pnma	5.475, 2.790, 11.467	504	566	484	239	111	238	228	236	233	327, 313 ^b , 329 ^c	175, 162 ^b , 162 ^c	445	0.273	1.560
Cr ₂₃ C ₆	Fm $\bar{3}m$	7.443	479			139			196			290, 283 ^b , 300 ^c	140, 145 ^b , 137 ^c	362	0.292	0.988
Fe ₃ C	Pnma	4.919, 6.738	441	371	322	26	148	144	183	160	212	249	102	270	0.320	1.304
HfC	Fm $\bar{3}m$	4.646	530			172			114			253, 236 ^d , 263 ^e	186, 166 ^d , 200 ^e	448	0.204	0.862
MoC	Fm $\bar{3}m$	4.375	662			113			187			345	163	422	0.296	0.623
NbC	Fm $\bar{3}m$	4.506	643			167			126			298, 285 ^d , 331 ^e	204, 167 ^d , 193 ^e	498	0.222	0.716
OsC	P $\bar{6}m2$	2.950, 2.727	429		869	82		17	396	252		392, 393 ^f	92, 82 ^f	255	0.392	2.024
ReC	Fm $\bar{3}m$	4.358	632			-79			256							
RuC	P $\bar{6}m2$	2.937, 2.680	408		745	94		45	319	225		344	99	271	0.369	1.829
SiC	Fm $\bar{3}m$	4.379	375			236			121			206	193	440	0.143	1.579
TaC	Fm $\bar{3}m$	4.475	711			173			150			337, 317 ^d , 357 ^e	216, 209 ^d , 214 ^e	534	0.236	0.698
TiC	Fm $\bar{3}m$	4.337	527			161			133			265, 257 ^d	176, 162 ^d	431	0.228	0.863
VC	Fm $\bar{3}m$	4.155	636			185			140			305, 307 ^d	210, 171 ^d	513	0.220	0.802
WC	P $\bar{6}m2$	2.919, 2.845	706		944	306		235	235	190		398	286	691	0.211	1.338
ZrC	Fm $\bar{3}m$	4.724	477			148			113			234, 217 ^d , 247 ^e	162, 124 ^d , 177 ^e	394	0.220	0.856

^aRef. [21], experimental results^bRef. [52], DFT with GGA, spin polarization not considered^cRef. [53], DFT with GGA, spin polarization considered^dRef. [54], DFT with GGA^eRef. [45], DFT with LDA^fRef. [55], DFT with GGA^{*} spin-polarization considered

Table 3 LCs (in Å) and elastic properties (C_{ij} , B , G and E in GPa) of nitrides at zero pressure

	SG	LCs	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}	B	G	E	ν	A
AlN	Fm $\bar{3}m$	4.067	419			303			169			252	232	533	0.148	1.850
BN	F $\bar{4}3m$	3.625	766			433			161			363	381	847	0.111	1.342
C ₃ N ₄	P6 ₃ /m	6.448, 2.422	822		1013	283		286	250	120		404	315	750	0.191	1.233
C ₃ N ₄	Fd $\bar{3}m$	4.795	901			200			88			359	283	672	0.188	0.542
CrN	Fm $\bar{3}m$	4.054	573			6			200			324, 325 ^a	78, 60 ^a	217	0.388	0.369
		4.150 [*]	490 [*]			60 [*]			141 [*]			257, 249 ^b	106, 150 ^b	279	0.319	0.534
Cr ₂ N	P $\bar{3}1m$	4.784, 4.404	472		404	161		156	160	235		290	144	369	0.287	0.855
Fe ₁₆ N ₂	I4/mmm	5.676, 6.244	305		320	80		82	115	138		190	85	221	0.306	0.865
Fe ₂ N	P $\bar{3}1m$	4.750, 4.317	350		338	103		99	153	210		243	92	245	0.331	0.965
Fe ₃ N	P6 ₃ 2	4.656, 4.317	307		315	101		85	137	140		196	91	237	0.298	1.105
Fe ₄ N	Pm $\bar{3}m$	3.671	385			64			175			245	80	217	0.352	0.787
GaN	Fm $\bar{3}m$	4.277	360			201			161			227	161	390	0.214	1.565
HfN	Fm $\bar{3}m$	4.532	614			116			122			286, 267 ^c , 306 ^d	168, 123 ^c , 185 ^d	422	0.254	0.576
InN	Fm $\bar{3}m$	4.723	281			116			115			171	103	257	0.249	1.233
IrN ₂	Pnnm	4.094, 4.929, 2.781	674	838	482	109	272	169	146	263	79	330, 347 ^e	210	520	0.237	0.560
MoN	Fm $\bar{3}m$	4.347	588			-43			224							
NbN	Fm $\bar{3}m$	4.453	648			75			134			306, 332 ^a , 354 ^d	148, 176 ^a , 134 ^d	381	0.292	0.438
OsN ₂	Pnnn	2.698, 4.955, 4.147	576	931	735	173	329	131	90	269	169	366, 362 ^e	241	592	0.230	0.417
Pd ₂ N	Pnnn	3.157, 5.149, 4.765	242	227	215	91	36	54	139	130	173	174	52	143	0.363	1.125
PtN	F $\bar{4}3m$	4.780	174			6			202							
PtN ₂	Pnnn	3.203, 4.872, 3.760	477	692	466	143	245	105	86	243	86	274, 286 ^e	180	443	0.231	0.435
RuN ₂	Pnnm	4.110, 4.927, 2.726	604	762	420	90	258	109	148	210	72	294	182	452	0.244	0.413
ScN	Fm $\bar{3}m$	4.497	411			168			118			216, 217 ^a	159, 153 ^a	383	0.204	1.102
Si ₃ N ₄	P6 ₃ /m	7.660, 2.925	400		521	99		112	176	103		232	125	317	0.272	1.302
Si ₃ N ₄	Fd $\bar{3}m$	5.506	692			233			84			286	261	601	0.150	0.793
TaN	Fm $\bar{3}m$	4.414	762			59			138			346, 320 ^a , 372 ^d	160, 84 ^d	417	0.299	0.335
TiN	Fm $\bar{3}m$	4.255	595			159			137			290, 269 ^a , 283 ^c	187, 189 ^a , 109 ^c	462	0.234	0.764
VN	Fm $\bar{3}m$	4.118	609			124			186			327, 325 ^a , 317 ^c	159, 185 ^a , 109 ^c	411	0.291	0.712
V ₂ N	P $\bar{3}1m$	4.901, 4.534	451		441	149		144	164	194		272	141	360	0.279	0.976
WN	P $\bar{6}m2$	2.864, 2.900	649		706	114		226	196	277		389	175	456	0.305	1.087

Table 3 (continued)

	SG	LCs	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}	B	G	E	ν	A
YN	Fm $\bar{3}m$	4.919	311						83			159	120	288	0.198	1.061
ZrN	Fm $\bar{3}m$	4.608	564			124			114			264, 263 ^b , 283 ^d	159, 150 ^a , 169 ^d	398	0.249	0.613

^aRef. [46], DFT with GGA, spin polarization not considered^bRef. [38], DFT with GGA, spin polarization considered^cRef. [54], DFT with GGA^dRef. [45], DFT with LDA^eRef. [56], DFT with GGA

* spin-polarization considered

Fig. 2 Relationship of B (G , E) and LCs ratio c/a for thirteen MB_2 -type borides. Solid lines are fitted curves and dashed ones are guides for eyes

For the seventeen carbides, eleven of them have the SG $Fm\bar{3}m$ (see Table 2 for details). The B of most carbides is usually higher than that of the counterpart borides, such as Ti-, V- and W-based compounds. From the group IV to VI, the B , G and anisotropy of the $3d$ – $5d$ TM carbides all increase. Within the SG $Fm\bar{3}m$, MoC has the highest B of 345 GPa, while TaC possesses the highest $G=216$ GPa and $E=534$ GPa. The $5d$ TM carbides OsC and WC have relative higher bulk moduli which are comparable with that of diamond (414 GPa), but the former gives quite small G and E as well as rather obvious anisotropy ($A=2.024$). The elastic constants of CrC label with * in Table 2 correspond to spin-polarized state; otherwise, it is non-magnetic state (the same for CrN in Table 3). We can see that the LCs increase by 9%, while the elastic properties decrease remarkably with spin polarization considered. However, no difference is found for Cr_3C_2 and $Cr_{23}C_6$ between magnetic and non-magnetic state. This abnormal phenomenon looks similar with CrN [38] and needs further study.

By comparing the elastic properties of the thirty-one nitrides from Table 3, the light element nitrides (cBN, C_3N_4) exhibit better elastic properties than the metal nitrides. The $P6_3/m-C_3N_4$ possesses the highest $B=404$ GPa, which is comparable with that of diamond (414 GPa), and the $P6_3/m-WN$ also owns a favorable $B=389$ GPa. Similar to the carbides, 12 binary nitrides (mainly group IV–VI TM ones) in Table 3 have the SG $Fm\bar{3}m$. The highest values of B , G and E among the $Fm\bar{3}m$ -structured are 346 GPa (TaN), 232 GPa (AlN) and 533 GPa (AlN), respectively. For the $3d$ – $5d$ TM nitrides, the values of B lie in the range of 300 ± 50 GPa and increase from group IV to VI. The elastic anisotropy of group VI compounds follows $Cr > Mo > W$, in contrary to the group IV and V ones. Recently, the orthogonal-structured

Fig. 3 Cross sections of Young's moduli distribution on the (001) plane (*ab* plane) for group IV–VI TM carbides **a** and nitrides **b**. WC and WN are excluded for hexagonal structure, and MoN for elastic instability. Horizontal and vertical directions correspond to *a* and *b*

axes of a cubic crystal. Blue circles are contour lines and numbers are values with unit of GPa for Young's moduli; the increment is 100 GPa

4d and 5d noble TMs Ir, Os, Pt and Ru nitrides have drawn much attention for their mechanical or functional properties [42, 49, 56]. Our calculations show their elastic properties are competitive with the group IV–VI TM nitrides; see details from Table 3. Again, clear difference is found for the LCs and elastic constants of CrN between magnetic and non-magnetic state. Zhou et al. [38] have discussed the influence of magnetic state on the elastic constants of CrN, and the spin polarization should be employed in first-principles calculations.

Based on the above-calculated results of the ninety compounds, the 5d TM phases ReB₂, WB, OsC, RuC, WC, OsN₂ and WN as well as TaN exhibit comparable bulk moduli

with cBN; the others all have smaller bulk moduli. Therefore, one efficient way for screening hard materials is the synthesis of new compounds via strong covalent-bonded light elements or 5d TMs with light elements. In addition, the fundamental elastic constants of these compounds can be further used to derive other elastic-related properties, such as Debye temperature [47].

3.2 Anisotropy and Bonding

The widely used group IV–VI TM compounds are representative among the ninety phases for their uniform cubic structure and considerable elastic properties. The elastic

Fig. 4 Correlation between the normalized Cauchy pressures $p = (C_{12} - C_{44})/B$ and the Pugh's modulus ratio $r = G/B$ for 86 elastically stable compounds **a** and group IV–VI TM phases **b**. Black dash line in **a** is the fitting curve

Table 4 Calculated SFEs at 0 K. The SFEs of SF1 are italic

	SFEs (mJ/m ²)		SFEs in studies (mJ/m ²)
	Cell shape fixed	Cell shape relaxed	
Diamond	277.5, <i>9167</i>	258.1	318 ^a , 279 ^b
cBN	183.8, <i>6515</i>	176.5	191 ^c
β-SiC	1.52	1.14	− 1.7 ^d
PtN	318.0	293.7	
HfB	− 26.2	− 46.6	
ZrB	42.4	25.8	
CrC	− 100.7 ^e , − 172.5 ^f	− 198.7 ^e , − 258.8 ^f	
HfC	1609	1604	
MoC	− 929.9	− 1211	
NbC	637.8	568.5	
ReC	− 1021	− 3206	
TaC	772.6	633.4	
TiC	1672, <i>3495</i>	−	
VC	895.5	892.6	
ZrC	1367	−	
AlN	4813	4453	
CrN	1112 ^e , 2775 ^f	425.4 ^e , 527.3 ^f	
GaN	3544	−	
HfN	234.5	297.9	
InN	1821	−	
NbN	− 130.0	− 677.5	
ScN	1889	−	
TaN	− 147.7	− 970.8	
TiN	1081, <i>1509</i>	−	1050 ^g
VN	91.0	− 329.1	
YN	1217	−	
ZrN	330.3	224.2	

^aRef. [62], DFT^bRef. [63], experimental result by transmission electron microscope^cRef. [64], experimental result by transmission electron microscope^dRef. [65], DFT^eSpin polarization considered in this study^fSpin polarization not considered in this study^gRef. [66], DFT

anisotropy could be visualized by plotting Young's moduli (E) versus crystal direction in cubic structure [46, 57]. The larger the difference between the maximum and minimum values of the E , the stronger the anisotropy of the structure. The cross sections (perpendicular to c axis of the crystal) of E surface for the group IV–VI TM carbides and nitrides are shown in Fig. 3, where horizontal and vertical directions correspond to a and b axes of cubic crystals. For both carbides and nitrides, along the a or b direction, the E is maximum, while minimum is along the bisector direction of a and b axes. From Fig. 3, the anisotropic character increases from group IV to group VI TM compounds. The group IV

TM (Ti, Zr and Hf) carbides are approximately isotropic, while group VI (Cr and Mo) carbides and nitrides show obvious elastic anisotropy. It should be also noted that these TM nitrides have stronger anisotropy than the counterpart carbides, especially for HfN, NbN and TaN. These anisotropy characters are in good agreement with the factors calculated from Eq. (8) (see A values in Tables 2, 3). Accordingly, discrepancies should be carefully considered in comparison between experimental and theoretical elastic properties for materials with strong anisotropy.

Based on the above-calculated elastic properties, the bonding characters can be analyzed by the normalized Cauchy pressures $p = (C_{12} - C_{44})/B$ and the Pugh's modulus ratios $r = G/B$. If p is negative and r is higher than 0.57, the material will appear to have covalent bonding; otherwise, it is metallic bonding [58–60]. Also, the lower the p value, the higher the r value and the more brittle the material. The relationship between p and r is plotted for the 86 elastically stable compounds (Fig. 4a) and group IV–VI TM phases (Fig. 4b). From Fig. 4a, most of these phases are distributed following the fitted curve (black dash line) $p = J^*r + K$, where constants $J = -1.62 \pm 0.08$ and $K = 1.00 \pm 0.05$. For borides and carbides, the group III–VI phases usually show covalent bonding and brittle characters, while group VII–X ones exhibit metallic bonding and ductile characters. For TM nitrides, the group III–IV phases have covalent bonding, while the others have metallic bonding. Although HfB and ZrB lie in the upper left region of Fig. 4b, all the group IV–VI TM borides can be regarded as covalent bonded. However, metallic bonding appears in the group V TM carbides as well as group VI TM carbides (besides WC) and nitrides. The origin of these bonding characters can be understood from electronic structure, which will be explored in our future work.

3.3 Stacking Fault Energies

Recent studies have confirmed that the Vickers hardness can increase from 90 to 120 GPa and even 200 GPa with single-crystalline, nano-grained and nano-twinned diamond [23]. The same phenomenon is also reported for cBN [22] and Fm $\bar{3}$ m-SiC (β-SiC) [24]. That is to say, these materials can be strengthened via grain refinement or twin defects. From this point of view, better elastic properties could be expected by introducing twins in the binary borides, carbides or nitrides. Twin formation tendency is strongly correlated with the SFEs, γ . It is easier for twin growth with lower SFE, such as β-SiC ($\gamma \sim 1$ mJ/m²) and silver ($\gamma \sim 18$ mJ/m²); and it is rather difficult for twin formation in materials with high SFEs, such as aluminum ($\gamma \sim 130$ mJ/m²) and diamond ($\gamma = 277$ mJ/m²). However, twins may form in high-SFE materials at certain conditions, e.g., high strain rate, high temperature and high pressure [23, 61].

Considering the twined diamond, cBN and β -SiC are face-centered cubic (FCC) crystals, and thus the SFEs of twenty-seven compounds with FCC structure (SG $F\bar{4}3m$ for diamond, cBN, β -SiC, PtN and $Fm\bar{3}m$ for the others) are calculated and listed in Table 4. Here, two regimes of relaxation are employed in the SFEs calculation, cell shape fixed and cell shape relaxed with the atom positions relaxed in both regimes. The SFEs of SF1 and SF2 configurations (illustrated in Fig. 1) have been tested for diamond, cBN, TiC and TiN. The energies of SF1 are italic in Table 4. We can see that the SFE2 is much lower than the SFE1 and indicates that SF2 is an energetically favorable configuration. Thus, only SF2 is considered for the other phases. With cell shape fixed regime, the calculated SFEs are in good agreement with the available data and slightly larger than the cell shape relaxed ones. Once the SFE is larger than 1000 mJ/m^2 , only the fixed regime is employed because there is little difference between the two regimes, e.g., HfC and AlN; see Table 4 for details. Nano-twinned diamond [23] can be fabricated from onion-like precursor. Thus, at certain circumstance, twins may form in PtN, ZrB, HfN, VN and ZrN, whose SFEs are lower or slightly higher than that of diamond ($\gamma = 277.5 \text{ mJ/m}^2$) from Table 4. Thus, the mechanical performance could be enhanced via twinning. However, it is difficult for twin formation in most of the carbides and nitrides, which have rather large SFEs, i.e., $\gamma > \gamma(\text{NbC}) = 637.8 \text{ mJ/m}^2$. The reason why several SFEs (HfB, CrC, MoC, ReC, NbN and TaN) are much below zero is that the energy of the faulted stacking sequence is lower than perfect FCC stacking configuration. In other words, a hexagonal structure, in which close-packed stacking sequence is the same as the faulted FCC stacking sequence, is more energetically stable than the FCC structure with the same atoms. For instance, the energy of one Ta atom plus one N atom in $P6_3/mmc$ -TaN is -22.112 eV , which is lower than -21.924 eV for $Fm\bar{3}m$ -TaN and thus results in negative SFE.

4 Conclusion

Enormous first-principles calculations are employed in the determination of elastic properties and SFEs of ninety binary borides, carbides and nitrides, and the calculations show reasonable agreement with the available data. Most of these compounds have a considerable bulk modulus more than 260 GPa, especially for the $5d$ TM ones (ReB₂, WB, OsC, RuC, WC, OsN₂, TaN and WN), in which the bulk moduli are comparable with cBN. Light element phases exhibit superior elastic properties than TM ones. Therefore, the synthesis of new compounds via strong covalent-bonded light elements or $5d$ TMs with light elements is an efficient way to be harder. The group IV–VI TM borides show covalent

bonding, while metallic bonding appears in the group VI TM carbides, the group VI TM nitrides and the group V carbides. The anisotropy characters are distinguishing for the group IV–VI TM carbides and nitrides. Another way for getting harder is introducing twin boundary defects into the materials. By comparing the calculated SFEs of twenty-seven cubic compounds, twins can be expected to form in ZrB, HfN, PtN, VN and ZrN, since their SFEs are lower or slightly higher than that of diamond.

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