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The crystal structures, phase stabilities, electronic structures and bonding features of iridium borides from first-principles calculations†

Jinquan Zhang,^a Yuanyuan Jin,*^a Chuanzhao Zhang,^b *a Yanqi Wang,^a Libiao Tang,^a Song Li,^a Meng Ju,^b Jingjing Wang,^b Weiguo Sun^b and Xilong Dou^e

We present results of an unbiased structure search for the lowest energy crystalline structures of various stoichiometric iridium borides, using first-principles calculations combined with particle swarm optimization algorithms. As a result, besides three stable phases of C2/m-Ir₃B₂, Fmm2-Ir₄B₃, and Cm-Ir₄B₅, three promising metastable phases, namely, $P2_1/m$ -Ir₂B, $P2_1/m$ -IrB, and Pnma-Ir₃B₄, whose energies are within 20 meV per atom above the convex hull curve, are also identified at ambient pressure. The high bulk modulus of 301 GPa, highest shear modulus of 148 GPa, and smallest Poisson's ratio of 0.29 for C2/m-Ir₃B₂ make it a promising low compressible material. C2/m-Ir₃B₂ is predicted to possess the highest Vickers hardnesses, with a Vickers hardness of 13.1 GPa and 19.4 GPa based on Chen's model and Mazhnik-Oganov's model respectively, and a high fracture toughness of 5.17 MPa m^{0.5}. The anisotropic indexes and the three-dimensional surface constructions of Young's modulus indicate that Ir–B compounds are anisotropic with the sequence of the elastic anisotropy of Ir₂B > Ir₈B > Ir₄B₅ > Ir₃B₄ > Ir₄B₃ > Ir₃B₂. Remarkably, these iridium borides are all ductile. We further find that the four Ir–B phases of $P2_1/m$ -Ir₂B, C2/m-Ir₃B₂, $P2_1/m$ -Ir_B, and Fmm2-Ir₄B₃ possess dominant Ir–B covalent bonding character, while strong B–B and Ir–B covalent bonds are present in Cm-Ir₄B₅ and Pnma-Ir₃B₄, which are responsible for their excellent mechanical properties.

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1 Introduction

With increasing demands for hard materials in industrial applications and the strict requirements in complex environments, transition metal borides have become the most important industrial materials because of their excellent wear resistance, ultra-incompressibility, high hardness, and high melting point. ¹⁻⁸ Previous experimental studies have shown that many transition metal borides such as ReB₂ (ref. 9) (48 GPa), OsB₂ (ref. 10) (35.2 GPa), CrB₄ (ref. 11) (48 GPa), WB₄ (ref. 12) (43.3 GPa), and MnB₄ (ref. 13) (37.4 GPa) have high hardness and can be synthesized under normal or low relative pressure through arc melting, making their production cost lower and

Crystal structure search has been widely applied to predict binary hard and superhard materials (i.e. compounds with Vickers hardness > 40 GPa) because it can search for a series of stable and metastable phases only with given components, which provides a powerful tool for the systematic exploration of binary transition metal borides.19 Therefore, previous researchers have systematically studied many binary transition metal borides by using structure search to find some borides with high hardness and fully understand the thermodynamic properties of the system.20-25 Although previous researchers have done a lot of research on the Y-B binary system for a long time, Ding et al. used CALYPSO to systematically study Y-B system and found a new stable phase $R\bar{3}m$ -YB₆ with the hardness of about 37 GPa. Besides, they also found that the previously high-temperature synthesized YB₄ is in metastable phase in the Y-B system.21 In addition, the systematic study of the compounds can also guide subsequent experiments and solve the uncertainty of boride structure caused by the difficulty in determining the position of lighter boron atoms in experiments. For example, A. N. Kolmogorov et al. have systematically studied the Fe-B system20 and found that the orthogonal

easier to expand. Notably, the combination of structure searching algorithms with first principles calculations, play a key role in understanding the origin of high hardness and in accelerating the discovery of some hard materials. 14-18

[&]quot;Department of Physics and Optoelectronic Engineering, Yangtze University, Jingzhou 434023, China. E-mail: scujyy@163.com; zcz19870517@163.com

^bSchool of Physical Science and Technology, Southwest University, Chongqing 400715, China

College of Computer and Information Engineering, Hubei Normal University, Huangshi 435002. China

^dCollege of Physics and Electronic Information, Luoyang Normal University, Luoyang 471022, China

^eInstitute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065, China

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intrinsic physical properties of these structures from the microscopic level.

structure oP10-FeB4 is metastable above the convex hull curve, which indicates that this compound may be stable at finite temperature. Subsequent high-temperature experiments show that orthogonal phase FeB4 is a potential superconductor and superhard material, and its hardness is 43-70 GPa.²⁶ Recent theoretical studies using USPEX, a global crystal structure search technique, have systematically studied the W-B system and have predicted a new stable compound, superhard tungsten pentaboride WB5, suggesting that the long-debated "WB4" and the newly predicted WB5 are actually the same material. 16,24 This finding better resolves the previous controversy over the structure of WB₄. Ir and Os are neighboring 5d transition metals in the periodic table and both have similar electronegativity, so Ir-B compounds were also considered as potential high hardness materials after the discovery of superhard OsB₂. Although previous theoretical and experimental studies have been carried out on the Ir-B system, the data on electronic properties and metastable phases of Ir-B compounds are quite limited, especially those close to convex hull curves of iridium boride, which may still have some problems in the study of metastable phases synthesized at high temperature.

For Ir-B system, iridium boride films with fractional stoichiometric ratios have attracted much attention due to their super-hard properties. Recently, iridium borides have attracted much attention because it is reported that IrB_{1,35} has Vickers hardness of 49.8-18.2 GPa under a load of 0.49 and 9.81 N, respectively, which is potential superhard material.27 Later, IrB_{1,1} film (0.4 μm) was deposited on a silicon dioxide substrate by pulse deposition technology, with Vickers hardness as high as 43 GPa.28 Subsequently, Zeilinger et al.22 and Wang et al.23 systematically studied the Ir-B phase diagram and the mechanical properties of the stable phase on the convex hull curve. In 2016, two groups successfully used a mechanochemical approach to synthesize two new iridium borides, namely, IrB2 and IrB, and found that IrB and IrB2 ceramic nanopowders may be an active catalyst material. 29,30 However, these two newly discovered borides have been proved to be metastable phases close to the convex hull curve. Previous systematic studies and synthesis of many metastable phases in Ir-B system have fully demonstrated that the study of metastable phases in Ir-B systems is very important. These metastable phases can usually be synthesized by selecting suitable precursors and controlling the quenching rate. However, no independent search for potential metastable structures of Ir-B system beyond known structure types has been performed to date, and there has been no systematic study of their mechanical properties, elastic anisotropy, bonding nature, and hardness. The goal of this work is to address these deficiency.

To find stable and metastable compounds that may not have been previously observed experimentally or computationally, we performed here an extensive study on binary iridium borides using the Crystal Structure Analysis by Particle Swarm Optimization (CALYPSO)^{31,32} method in combination with first-principles calculations. Finally, we reproduce the previously reported three stable structures and find three metastable structures that may be synthesized at high temperature, and comprehensively explore the structural characteristics and

2 Computational methods

To comprehensively search for the stable and metastable structures in the Ir–B binary system under atmospheric pressure, our structure-searching simulations are based on a particle swarm optimization algorithm in conjunction with *ab initio* total-energy calculations, as conducted in CALYPSO code. The significant feature of this code is that it can quickly predict the most stable and metastable 2D and 3D solid-state structures only requiring chemical compositions of a given compound at given external conditions and the superior efficiency of this methodology has been verified on various systems, spanning from elements to binary and ternary compounds. The formula units (f.u.) per simulation cell were performed for stoichiometries $Ir_m B_n$ varying from $Ir_3 B$ to IrB_3 .

All the following structural relaxations and electronic structure calculations were carried out with the utilization of density functional theory within the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional as implemented in the Vienna ab initio simulation package (VASP).38,39 The electron-ion interaction was described via a projector augmented wave (PAW) potentials with 5d⁷6s² and 2s²2p¹ valence electron for Ir and B, respectively.40 A plane wave cutoff energy of 600 eV and proper Monkhorst-Pack k-meshes were selected to guarantee that all the enthalpy calculations were well converged to better than 1 meV per atom. 41-43 To probe into the dynamical stability of $Ir_m B_n$ compositions, the phonon dispersion curves were calculated through the direct supercell approach as implemented in the Phonopy code. 44 In addition, the electron localization function (ELF)45 and Bader charge46 were also computed within the VASP code. To analyze the interatomic interaction and chemical bonding, the crystal orbital Hamilton populations (COHP) were calculated using the LOBSTER. 47 The independent single-crystal elastic constants could be ascertained on the basis of the stress tensor generated by employing a small strain to an optimized unit cell. Furthermore, the bulk modulus (B), shear modulus (G), Young's modulus (E), and Poisson's ratio (ν) were thus determined by the Voigt-Reuss-Hill (VRH) approximation.48 Vickers hardness was estimated according to the Chen49 $(H_v^C(GPa))$ and Mazhnik-Oganov⁵⁰ $(H_v^{MO}(GPa))$ models. Fracture toughness was calculated using the empirical Mazhnik-Oganov model (K_{IC}) .

Finally, for the purpose of fully describing the elastic anisotropy behavior of the considered structure in the Ir–B binary system, we constructed the three-dimensional model of Young's modulus by using the elastic anisotropy measurement (ElasticPOST) program.⁵¹

3 Results and discussion

3.1 Crystal structures and stability

To determine the stable and metastable phases of Ir-B compounds at ambient pressure, we have implemented

structure searches using the CALYPSO method on iridium borides with various Ir_mB_n compositions at considered pressures of 1 atm. This crystal structure search successfully reproduces the experimental structures of Pnma-IrB and $P6_3/mmc$ -IrB $_2$ as the lowest ground state energy phases and the other theoretical ground phases of C2/m-Ir $_3B_2$, Fmm2-Ir $_4B_3$, and Cm-Ir $_4B_5$, thus providing important support for the reliability of the present structure searches. Pegative formation enthalpy shows that the synthesis of the substance through the reference phase is an exothermic process, and the exothermic reaction is easy to occur in nature. The formation enthalpies can be calculated with the following equation:

$$\Delta H = \frac{E(\operatorname{Ir}_{x} \mathbf{B}_{y}) - xE(\operatorname{Ir}) - yE(\mathbf{B})}{x + y} \tag{1}$$

Herein, ΔH is the formation enthalpy per atom for a compound of this stoichiometry, E(IrxBy) is the total energy per formula unit of the compound, and E(Ir) and E(B) represent the Ir and B ground states with the cubic phase⁵² (space group: $Fm\bar{3}m$) and α -rhombohedral streutue,⁵³ respectively. Subsequently, we use the formation enthalpy to evaluate the thermodynamic stability of iridium borides. The calculated lattice parameters, cell volume, total energy and formation enthalpy for the lowest energy structures and the selected metastable structures of each considered stoichiometry of the Ir-B system are tabulated in Table 1, in company with the previously experimental and theoretical results. On the basis of the formation enthalpies, the convex hull of the Ir-B binary system under atmospheric pressure is constructed as displayed in Fig. 1. The whole structural information for the lowest energy phases of each component considered in the binary Ir-B system under ambient pressure is listed in Table S1 of the ESI.† The

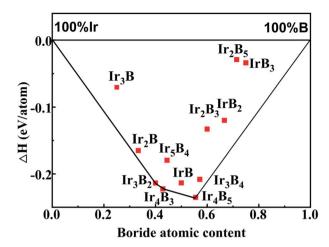


Fig. 1 The predicted formation enthalpy with respect to solid Ir and B for various Ir-B stoichiometries under atmospheric pressure. The solid line represents the ground state convex hull.

convex hull of these points then connects the structures with the lowest formation enthalpies among all stoichiometries, and any structures exactly located on the convex hull are deemed as energetically stable, both against decomposition into other elements or any combination of other binary phases, and thus experimentally synthetic. Furthermore, it should be specially pointed out that vibration effects may modify the convex hull curve at high temperatures, bringing out some structures that slightly deviate from the convex hull and approach to the convex hull. Therefore, it is extremely important to probe into not only the stable phases on the convex hull in Fig. 1, but also the metastable phases close to the convex hull curve. As presented in Fig. 1, it is obviously

Table 1 Calculated lattice parameters, a-axis, b-axis and c-axis (Å), cell volume V (Å 3), the total energy (eV per atom), and formation enthalpies per atom ΔH (eV per atom) for the relevant structures of various components of Ir-B system under ambient pressure, compared with experimental and theoretical consequences

Phase	Space group	a (Å)	<i>b</i> (Å)	c (Å)	$V(\mathring{A}^3)$	Total energy	ΔH
Ir ₃ B	$P\bar{6}m2$	2.794	2.794	7.512	50.776	-8.386	-0.073
Ir_2B	$P2_1/m$	5.699	2.803	4.736	74.600	-8.297	-0.163
	$Cmcm^{22}$	2.783	4.833	10.764	144.777	-8.278	-0.143
Ir_3B_2	C2/m	7.500	2.860	8.605	119.573	-8.205	-0.214
Ir_4B_3	Fmm2	5.659	5.731	10.020	324.942	-8.154	-0.224
Ir_5B_4	$P6_3/mmc$	3.521	3.521	18.957	203.535	-8.077	-0.181
IrB	$P2_1/m$	6.723	3.926	3.555	92.714	-7.990	-0.214
	$Pnma^{29}$	4.421	2.863	7.026	88.927	-7.990	-0.214
	Cmcm	4.036	5.850	3.926	92.694	-7.990	-0.213
	$P\bar{6}m2^{22}$	3.051	3.051	2.713	21.876	-7.966	-0.190
Ir_4B_5	Cm	10.623	2.902	12.373	189.252	-7.894	-0.236
Ir_3B_4	Pnma	16.266	2.962	6.028	290.436	-7.832	-0.208
Ir_2B_3	$P6_3/mmc$	3.124	3.124	12.184	102.992	-7.695	-0.132
IrB_2	C2/m	7.422	2.856	5.898	115.360	-7.544	-0.125
	Pnma	3.151	4.543	4.040	57.825	-7.540	-0.121
	$Pmmn^{56}$	5.586	2.983	6.818	113.619	-7.515	-0.095
	$P6_3/mmc^{29}$	3.075	3.075	7.054	57.767	-7.471	-0.052
Ir_2B_5	R3m	2.976	2.976	24.747	189.793	-7.347	-0.030
IrB ₃	$Pnma^{22}$	2.923	2.923	4.652	34.417	-7.275	-0.034
~	$P\bar{6}m2$	9.875	3.126	4.571	141.075	-7.242	-0.001

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found that the convex hull of Ir–B binary system contains three stable phases indicated as ${\rm Ir_3B_2}$ (C2/m), ${\rm Ir_4B_5}$ (Fmm2), and ${\rm Ir_4B_5}$ (Cm). Besides the stable structures on the convex hull, three metastable phases, ${\rm Ir_2B}$ ($P2_1/m$), ${\rm IrB}$ ($P2_1/m$), and ${\rm Ir_3B_4}$ (Pnma), are very close to the convex hull curve, whose energies are 15 meV per atom, 17 meV per atom and 16 meV per atom above the convex hull curve, respectively. These three meta-

the first time and may be synthesized at high temperature.²⁵ We below focus on the structural, mechanical and anisotropy, and electronic properties, bonding characters and hardness for these six considered crystals.

stable phases near the convex hull curve were discovered for

Starting from the phase with low boron content, each phase is discussed separately. For Ir₂B, the orthogonal Cmcm phase is considered to be the ground state phase by previous theory. By our method, we have reconstructed the orthogonal Cmcm phase well.23 Interestingly, our present calculations uncover a new crystal P2₁/m-Ir₂B, which is 0.019 eV per atom lower than the former. From Fig. 2a, each B atom is bonded with six Ir atoms, forming a trigonal prism (Ir₆B). By stacking the Ir₆B building blocks in the way of sharing one edge of the trigonal prism, the trigonal-prism chain is constructed. In the connected Ir₆B triangular prism, the Ir-B bond lengths vary between 2.14 and 2.20 Å, which is close to the strong covalent Ir-B bond of P6₃/ mmc-IrB₄ (ref. 54) (2.189 Å), stating that there exists a strong covalent bond between Ir and B in P2₁/m-Ir₂B. Furthermore, the distance of the nearest B-B bonds is 4.6 Å, showing that there is no B-B interaction. For the stable C2/m-Ir₃B₂ polycrystal (see Fig. 2b), there are two layers of iridium atoms along the c-axis sandwiched with a double layer of graphite-like Ir/B rings. In the connected bilayer graphite-like Ir/B rings, the Ir-B distances range from 2.15 Å to 2.19 Å are close to that of the potential hard materials m-IrB₂ (2.18 Å) with a theoretical Vickers hardness of 13.82 GPa.55

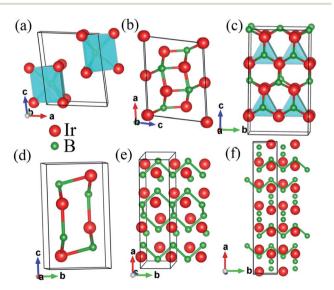


Fig. 2 Crystal structures of the six considered polymorps at ambient pressure. (a) $P2_1/m$ -Ir₂B, (b) C2/m-Ir₃B₂, (c) Fmm2-Ir₄B₃ (d) $P2_1/m$ -IrB, (e) Cm-Ir₄B₅ and (f) Pnma-Ir₃B₄. The red and green spheres represent the Ir and B atoms, respectively.

As shown in Fig. 2c, it is worth noting that the Fmm2-Ir₄B₃ structure has an alternating layered arrangement structure of B–Ir–B–Ir along the c-axis, and the layers are connected by Ir₆B prism building blocks. In the alternating B–Ir–B–Ir layers, the distances between the nearest Ir–B bonds are all less than the sum (2.25 Å) of covalent radii of the B atom (rB = 0.84 Å) and Ir atom (rIr = 1.41 Å). In particular, the minimum distance between B–B bonds is 4.03 Å, which is much larger than the possible bonding distance.

Subsequently, for IrB with a stoichiometric ratio of 1:1, previous theoretical calculations report three thermodynamically stable structures (Pnma,56 Cmcm,22 and P6m2 (ref. 23)). Intriguingly, the present calculations uncover a novel ground state phase P2₁₁/m-IrB, whose formation enthalpy is about 0.024 eV per atom lower than that of the $P\bar{6}m2$ -IrB phase, as summarized in Table 1. Surprisingly, the formation enthalpy of the P2₁/m-IrB structure is closely equal to that of Pnma-IrB synthesized in the above experiments at ambient pressure or Cmcm-IrB. As displayed in Fig. 2d, the P2₁/m-IrB crystal is composed of the twisted eight-membered ring formed by the alternating connection of Ir and B atoms. In an eight-membered ring, the maximum distance of Ir-B on the eight sides is 2.17 Å, and the minimum distance is 2.11 Å. The average Ir-B bond length of the P2₁/m-IrB is smaller than Ir-B (2.16 Å) covalent bonds in the Pnma-IrB under ambient pressure, indicating relatively strong Ir-B interactions.

At 1 < B/Ir < 2, the 1D B-ribbons are adopted by the lowestenergy structures of Cm-Ir₄B₅ and the metastable structure of Pnma-Ir₃B₄ at zero temperature, as shown in Fig. 2e and f. The distances between B–B bonds are respectively 2.00 Å and 2.02 Å in the 1D B-ribbons, which are very close to that of the potential hard materials C2/m-VB₃ of B–B bond distance (1.764–1.912 Å), indicating the existence of a strong B–B bond.⁵⁷ Besides the 1D B-ribbons, we also found the graphene-like B-sheet with short sides of 1.89 Å and long sides of 2.00 Å in Cm-Ir₄B₅, which is shorter than the high-pressure synthesis of β -Ir₄B₅ (2.122 Å).⁵⁸

In general, it is worth noting that the distances of the nearest neighbor Ir–B bonds in these six considered structures are all smaller than the sum (2.25 Å) of the covalent radii of the B atom (rB = 0.84 Å) and the Ir atom (rIr = 1.41 Å), demonstrating the strong covalent bonding between Ir and B in these six considered phases. However, with increasing B concentration, the number of Ir–B covalent bonds decreases, and strong B–B covalent bonds gradually appear for borides with 1 < B/Ir < 2.

As we all know, a crystal is dynamically stable if its potential energy always increases against any combinations of atomic displacements in the equilibrium state, which is given by: $\frac{\partial \Phi}{\partial r_\alpha(l\kappa)} = 0.$ In other words, this is equivalent to the condition

that all phonons have real and positive frequencies. Phonons reflect the quantized properties of lattice vibration energy, which can be measured by phonon dispersion curve and phonon density of states.⁵⁹⁻⁶² Therefore, to clarify the dynamical stabilities of these six considered phases, their phonon spectra and phonon density of states were also calculated, as depicted in Fig. 3. From Fig. 3, it can be obviously found that there are no virtual phonon frequencies in the entire Brillouin zone, which

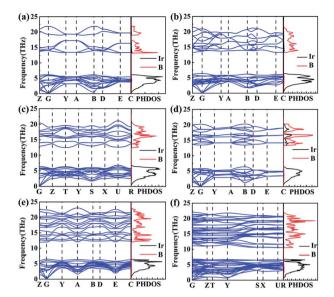


Fig. 3 Calculated phonon dispersion curves and projected phonon density of states (PDOS) of (a) $P2_1/m$ -Ir₂B, (b) C2/m-Ir₃B₂, (c) Fmm2-Ir₄B₃ (d) $P2_1/m$ -IrB, (e) Cm-Ir₄B₅ and (f) Pnma-Ir₃B₄ at ambient pressure.

proves that these six considered crystals are dynamically stable under environmental pressure. Moreover, the phonon bands for these six considered phases can be divided into two independent regions: the high-frequency mode mainly corresponds to the vibration of the boron atoms, while the low-frequency region is mainly related to the vibration of iridium atoms. This phenomenon stems from the larger atomic mass of the iridium atom than that of the boron atom.

3.2 Mechanical stabilities, mechanical properties and hardness

Elastic properties (such as elastic constants, elastic modulus, etc.) are essential for us to understand the deformation behavior of solids under the action of external forces, and can provide a deeper understanding of the macroscopic mechanical behavior, which is helpful to evaluate the mechanical properties of materials. The elastic constants of six considered phases were computed from the strain–stress method, along with previous results, which are collected in Table 2. The obtained elastic constants of C2/m-Ir $_3B_2$, Fmm2-Ir $_4B_3$ and Cm-Ir $_4B_5$ in Table 2, as well as the calculated bulk modulus, B, shear modulus, G, and Young's modulus, E, as listed in Table 3, are in good agreement with other available theoretical results, suggesting that the calculations in the present work are reasonable. 22,23

In addition, the mechanical stability of a crystal can be assessed through elastic constants. As summarized in Table 2, all the six considered phases meet the respectively mechanical stability criterion, suggesting the mechanical stabilities for these six considered structures under ambient pressure. Moreover, the C_{11} , C_{22} , and C_{33} values of six crystals (except $P2_1/m$ -IrB) can be compared with that of the potential superhard material TiB₂ (39.6 GPa), which implies that these five substances have larger incompressibility along the a-, b-, and c-axes. In general, the

Table 2 Calculated elastic constants C_{ij} (GPa) for the six considered structures in the Ir–B binary system

Phase	Space group	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}
Ir ₂ B	$P2_1/m$	522	540	516	169	46	68	150	143	198
Ir_3B_2	C2/m	475	490	481	174	184	130	206	249	180
Ir_3B_2	$C2/m^{22}$	479	507	479	128	171	200	202	248	180
Ir_4B_3	Fmm2	473	603	456	90	93	119	176	199	228
Ir_4B_3	Fmm2 (ref. 22)	486	655	473	96	101	112	165	215	185
IrB	$P2_1/m$	291	297	338	139	123	103	127	218	163
P ₁ -IrB	Pnma ⁵⁶	514	368	438	55	227	106	108	333	183
Ir_4B_5	Cm	474	424	518	88	167	76	161	216	158
Ir_4B_5	Cm^{23}	494	438	514	85	104	166	131	213	153
Ir_4B_5	Cm^{16}	519	459	548	112	178	88	150	218	177
α -Ir ₄ B ₅	$C2/m^{58}$	373	303	303	50	125	58	150	160	217
β -Ir ₄ B ₅	Pnma ⁵⁸	482	390	433	112	102	60	170	122	250
Ir_3B_4	Pnma	577	419	588	75	148	76	130	168	232
IrB_2	$P6_3/mmc^{56}$	326		705	124				198	248

elastic constant C_{44} is related to the resistance to shear deformation and most important parameter that indirectly determines the hardness of solid indentation.⁶⁴ Second, it can be found that C2/m-Ir₃B₂ has the largest C_{44} , which is much larger than the theoretical values of P₁–IrB, α -Ir₄B₅, β -Ir₄B₅ and $P6_3/mmc$ -IrB₂ synthesized experimentally, indicating that it exhibits higher hardness than the other iridium borides.

Materials with high bulk modulus usually have strong resistance to uniform compression. As shown in Table 3, the calculated bulk modulus ranges from 192 to 303 GPa, close to that of common hard materials such as ZrB₂ (220-245 GPa)⁶⁵ and TiB₂ (261 GPa), 63 but less than that of superhard materials ReB₂ (383 GPa), and WB₄ (553 GPa), indicating their strong ability to resist volume deformation. Among all the Ir-B compounds, C2/m-Ir₃B₂ and Fmm2-Ir₄B₃ have the highest bulk modulus (~300 GPa), which is larger than the theoretical values of P₁-IrB, α-Ir₄B₅, β-Ir₄B₅ and P6₃/mmc-IrB₂ reported by experiments, indicating that these two materials have the best incompressibility in Ir-B system. It is worth noting that some previous studies have shown that the bulk modulus may be directly related to the valence electron density (VED).66 As for the iridium boride compounds, it appears that the general trend of the bulk modulus is consistent with that of VED (except for P2₁/ m-Ir₂B) and the bulk modulus increases gradually with increasing VED.

Generally speaking, the larger value of the shear modulus also indicates that the orientation bonds between atoms are more obvious.⁶⁷ It is well known that the shear modulus of a material quantifies its resistance to shear deformation and is a more relevant predictor of material hardness than bulk modulus. The shear modulus of *C2/m*-Ir₃B₂ is 148 GPa, which is close to that of hard superconducting material NbN⁶⁸ (159.9 GPa) and larger than that of other Ir–B compounds. It is expected that Ir₃B₂ will resist shear strain to a large extent and has higher hardness than other Ir–B compounds.

Young's modulus, called the tensile modulus, is defined as the ratio of tensile stress to tensile strain in the elastic (linear) part of the stress-strain curve. When the value is large, the material is stiffer. The Young's modulus is also an important

Table 3 The calculated the bulk modulus B (GPa), shear modulus G (GPa), Young's modulus E (GPa), B/G, Poisson's ratio ν , valence electron densities VED (e Å $^{-3}$), hardness H_{ν}^{C} (GPa), hardness H_{ν}^{MO} (GPa) and the fracture toughness E (MPa m $^{0.5}$) for the six considered structures in the Ir $^{-1}$ B binary system

Phase	Space group	В	G	E	B/G	ν	VED	$H_{ m v}^{ m C}$	$H_{ m v}^{ m MO}$	$K_{\rm IC}$
Ir_2B	$P2_1/m$	255	96	256	2.66	0.33	0.563	6.2	14.0	3.66
Ir_3B_2	C2/m	301	148	381	2.04	0.29	0.552	13.1	19.4	5.67
Ir_3B_2	$C2/m^{22}$	302	150	386						
Ir_4B_3	Fmm2	303	118	314	2.57	0.33	0.554	7.7	17.2	6.15
Ir_4B_3	Fmm2 (ref. 22)	303	127	335						
IrB	$P2_1/m$	192	81	213	2.38	0.32	0.518	6.5	10.7	3.37
P ₁ -IrB	Pnma ⁵⁶	274	124	323	2.21		0.540			
Ir_4B_5	Cm	274	112	297	2.44	0.32	0.539	10.6	17.1	5.18
Ir_4B_5	Cm^{22}	269	125	325						
α -Ir ₄ B ₅	$C2/m^{58}$	225	63	180		0.37		4.5		
β -Ir ₄ B ₅	$Pnma^{58}$	265	99	266		0.33		8.5		
Ir_3B_4	Pnma	290	120	316	2.42	0.32	0.537	8.7	17.0	5.78
IrB_2	$P6_3/mmc^{56}$	283	113	299	2.50					

parameter for measuring the stiffness of a material in addition to the bulk modulus and shear modulus. When the value is large, the material is stiffer. From Table 3, the Young's modulus (381 GPa) of C2/m-Ir₃B₂ is the highest, comparable to that of the well-known hard material ZrC, ⁶⁹ indicating that C2/m-Ir₃B₂ has a higher hardness than the other Ir–B compounds. Poisson's ratio is an important parameter to describe the degree of directionality for the covalent bonding. Of all the phases considered, the C2/m-Ir₃B₂ has the smallest Poisson's ratio, which suggests that strong directional bonding exists in it and thus could be a potentially hard material. All of these excellent mechanical properties strongly suggest that C2/m-Ir₃B₂ is a potential candidate for hard material.

According to the standard of Pugh,⁷⁰ the toughness or brittle behavior of a solid can be estimated by the value of B/G. If B/G > 1.75, the material shows toughness and *vice versa*, if B/G < 1.75, the material shows brittleness. In the current situation, the B/G values of several compounds are all higher than 1.75. Therefore, these six compounds exhibit toughness behavior.

The hardness of a material is an important parameter to evaluate the performance of a material, especially in industries such as cutting. As shown in Table 3, the C2/m-Ir₃B₂ has the highest hardness, regardless of the use of either Chen's model or Mazhnik-Oganov's model. It can be seen that the calculated theoretical hardness of the C2/m-Ir₃B₂ is 13.1 and 19.4 GPa based on Chen's model and Mazhnik-Oganov's model, which is close to that of commonly used hard materials like, for example, RuB₂¹ (15.1 GPa) or Al₂O₃⁷¹ (17.8 GPa). It is consistent with result predicted from the elastic constant C_{44} , shear modulus and Young's modulus. The fracture toughness of Fmm2-Ir₄B₃, Pnma-Ir₃B₄ and C2/m-Ir₃B₂ are 6.15 MPa m0.5, 5.78 MPa m^{0.5}, and 5.67 MPa m^{0.5}, respectively, which is higher than that of WC⁷² (5.37 MPa m^{0.5}). The results show that Fmm2-Ir₄B₃, Pnma-Ir₃B₄ and C2/m-Ir₃B₂ have strong resistance to fracture propagation.

3.3 Anisotropy properties

Elastic anisotropy is an important physical property of materials. It not only plays a vital role in technical and industrial applications, but also reflects the arrangement of atoms along the corresponding direction to a certain extent. The general elastic anisotropy index and the anisotropy percentage of crystals with any symmetry are defined as follows:⁷³

$$A^{\rm U} = 5\frac{G_{\rm V}}{G_{\rm R}} + \frac{B_{\rm V}}{B_{\rm R}} - 6 \ge 0 \tag{2}$$

$$A_1 = \frac{4C_{44}}{C_{11} + C_{33} - 2C_{13}} \tag{3}$$

$$A_2 = \frac{4C_{55}}{C_{22} + C_{33} - 2C_{23}} \tag{4}$$

$$A_3 = \frac{4C_{66}}{C_{11} + C_{22} - 2C_{12}} \tag{5}$$

For an isotropic solid, its A^U is zero. The degree of anisotropy is shown by the deviation from zero. The greater the deviation from zero, the higher the degree of anisotropy of the material. In addition, the shear anisotropy constant can reflect the anisotropy of solids on different planes. For isotropic crystals, the values of A_1 , A_2 , and A_3 are equal to 1, and for any crystal less than or greater than 1, the degree of shear anisotropy of the crystal is indicated. Both the anisotropy index and the shear anisotropy factor are listed in Table 4.

Table 4 The calculated universal anisotropic index (A^U) , shear anisotropic factors $(A_1, A_2, \text{ and } A_3)$ for the six considered structures in the Ir-B binary system

Phase	Space group	A^{U}	A_1	A_2	A_3
Ir_2B	$P2_1/m$	5.51	0.90	0.28	0.36
Ir_3B_2	C2/m	0.27	1.52	1.20	0.94
Ir_4B_3	Fmm2	0.45	0.57	0.79	0.66
IrB	$P2_1/m$	3.60	2.88	1.59	1.23
Ir_4B_5	Cm	1.24	0.63	1.07	0.53
Ir_3B_4	Pnma	0.96	0.36	1.09	0.41

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For Ir-B compounds, the index A^{U} order in Table 4 is $Ir_2B >$ $IrB > Ir_4B_5 > Ir_3B_4 > Ir_4B_3 > Ir_3B_2$. The results show that among Ir-B compounds, Ir₂B has the highest elastic anisotropy, while Ir₃B₂ has the lowest elastic anisotropy. For the shear anisotropy constant, the values of the parameters A_1 , A_2 , and A_3 indicate that the anisotropy of Ir-B depends on the direction. Ir₂B has the largest absolute values $(1 - A_2)$ and $(1 - A_3)$, while Ir₃B₂ and Ir₄B₃ have smaller absolute values. This indicates that Ir-B compounds have the strongest anisotropy on the (010) and (001) planes, while Ir₃B₂ and Ir₄B₃ have the opposite results. For the Ir_2B compound, the value of A_1 is close to 1. This shows that Ir_2B is isotropic along the (100) plane. In addition, Ir₃B₂ also exhibits isotropy on the (001) plane.

The three-dimensional surface model can more intuitively describe the anisotropic behavior of solid elasticity. The threedimensional pattern of the reciprocal direction dependence of Young's modulus of the Ir-B compounds is different due to its different crystal structure. For different crystal structures of Ir-B compounds, there are different expressions for the constructing surfaces of Young's modulus.74

For monoclinic structure,

$$\frac{1}{E} = l_1^4 S_{11} + 2l_1^2 l_2^2 S_{12} + 2l_1^2 l_3^2 S_{13}
+2l_1^3 l_3^2 S_{15} + l_4^2 S_{22} + 2l_2^2 l_3^2 S_{23}
+2l_1^2 l_2^2 S_{25} + l_3^4 S_{33} + 2l_1 l_3^3 S_{35}
+l_2^2 l_3^2 S_{44} + 2l_1 l_2^2 l_3 S_{46} + l_1^2 l_3^2 S_{55} + l_1^2 l_2^2 S_{66}$$
(6)

For orthorhombic structure,

$$\frac{1}{E} = l_1^4 S_{11} + l_2^4 S_{22} + l_3^4 S_{33}
+ 2l_1^2 l_2^2 S_{12} + 2l_1^2 l_3^2 S_{13} + 2l_2^2 l_3^2 S_{23}
+ l_2^2 l_3^2 S_{44} + l_1^2 l_3^2 S_{55} + l_1^2 l_2^2 S_{66}$$
(7

Sijs are the elastic compliance constants and are shown in Table S2.† Fig. 4 displays the constructing surfaces for Young's modulus. The isotropic system will display a 3-dimensional sphere. The greater the deviation from the sphere, the higher the degree of anisotropy. In Fig. 4a, the 3D surface structure of Ir₂B is longer along the y axis than other compounds, while the surface structure along the x and z axes is more compressed than other compounds. The results show that the monoclinic structure of Ir₂B has the highest degree of anisotropy. In Fig. 4b, the 3D surface structure of the monoclinic Ir₃B₂ is closest to the sphere among all the structures, indicating that the anisotropy of Ir₃B₂ is the smallest. According to the three-dimensional surface structure, we can summarize the elastic anisotropy order of Ir-B compounds ($Ir_2B > IrB > Ir_4B_5 > Ir_3B_4 > Ir_4B_3 > Ir_3B_2$). This order is consistent with the result obtained by the anisotropy constant A^{U} .

Electronic properties and chemical bonding

To further analyze the electronic properties of these Ir-B configurations, we calculated their electronic band structure and electronic density of states (DOS) (see Fig. S1† and 5). As

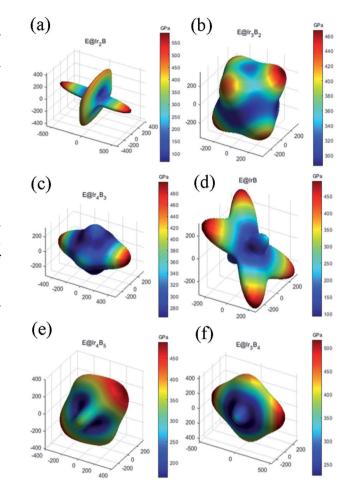


Fig. 4 Three-dimensional Young's modulus for (a) P2/1/m-Ir2B, (b) C2/m-Ir₃B₂, (c) Fmm2-Ir₄B₃ (d) $P2_1/m$ -IrB, (e) Cm-Ir₄B₅ and (f) Pnma-Ir₃B₄ under ambient pressure.

shown in the electronic band structure of Fig. S1,† these six phases have a strong overlap between the conduction band and the valence band, showing metallic characteristics. This can also be confirmed by the finite electron density of states of the Fermi level in Fig. 5. Moreover, in Fig. 5b and d-f, a typical feature in the TDOS can be seen that there is a deep valley at Fermi level for these compounds, that is, the presence of a socalled "pseudogap", which represents a borderline between the bonding and antibonding orbitals.75 The presence of the pseudogap enhances the stability of the compounds.

To gain further insights into the chemical bonding nature in the six considered phases, we calculate the electron localization function (ELF), which can make a description of the bond type between atoms: large ELF values (>0.5) corresponds to the electrons of perfect covalent bonds or lone pairs, while smaller ELF values (<0.5) correspond to ionic or metallic bonds. As seen in Fig. 6, it is worth mentioning that these six crystals display a common feature of the ELF that the high electron localization can be seen between Ir and adjacent B atoms, implying the strong covalent bonding of Ir-B. Besides, from Fig. 6e and f, we can also clearly see high electron localization in regions between adjacent B atoms, which indicated the high covalence

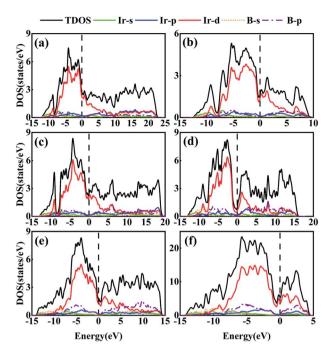


Fig. 5 Calculated electronic density of states for (a) $P2_1/m$ -Ir $_2$ B, (b) C2/m-Ir $_3$ B $_2$, (c) Fmm2-Ir $_4$ B $_3$ (d) $P2_1/m$ -IrB, (e) Cm-Ir $_4$ B $_5$ and (f) Cm

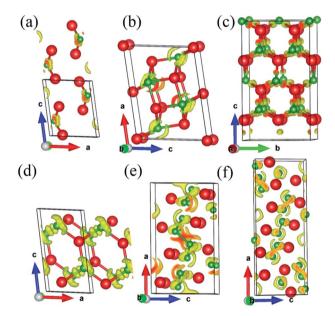


Fig. 6 ELFs of the (a) $P2_1/m$ -Ir $_2$ B, (b) C2/m-Ir $_3$ B $_2$, (c) Fmm2-Ir $_4$ B $_3$ (d) $P2_1/m$ -IrB, (e) Cm-Ir $_4$ B $_5$ and (f) Pnma-Ir $_3$ B $_4$ (isovalue = 0.65).

of B–B bonding. According to the periodic law, the electronegativity value of the boron element (2.00) is less than the electronegativity value of the iridium element (2.2), which means that the charge should be transferred from the B atom to the Ir atom. Therefore, to analyze the actual charge distribution between B and Ir atoms, we explicitly measure the Bader charges of the B and Ir atoms for all six crystals, as summarized in Table 5. The average of transferred electrons charges from B

Table 5 Calculated Bader charges of Ir and B atoms in six considered phases. δ denotes the amount of charge transferred from B atom to the Ir atom

Phase	Space group	Atom	Charge value (e)	δ (e)
Ir ₂ B	$P2_{1}/m$	Ir	9.15	-0.15
-	•	В	2.70	0.30
Ir_3B_2	C2/m	Ir	9.15	-0.15
		В	2.78	0.22
Ir ₄ B ₃	Fmm2	Ir	9.17	-0.17
		В	2.77	0.23
IrB	$P2_1/m$	Ir	9.41	-0.41
		В	2.59	0.41
Ir_4B_5	Cm	Ir	9.35	-0.35
		В	2.72	0.28
Ir ₃ B ₄	Pnma	Ir	9.33	-0.33
- •		В	2.75	0.25

to the Ir atoms are about 0.3 e, 0.22 e, 0.23 e, 0.41 e, 0.28 e, 0.25 e for $P2_1/m$ -Ir $_2$ B, C2/m-Ir $_3$ B $_2$, Fmm2-Ir $_4$ B $_3$, $P2_1/m$ -IrB, Cm-Ir $_4$ B $_5$, and Pnma-Ir $_3$ B $_4$. Therefore, there is a small amount of charge transfer from B to the Ir atoms, indicating a covalent bonding character.

Finally, we calculated their integrated-crystal orbital Hamilton populations (ICOHPs) to depict the strength of chemical bonds in the six Ir-B phases by counting the energy-weighted population of wave function between two atomic orbitals (see Table S3†). The calculated ICOHP values (\ge −2.28 eV) of Ir-B in the six iridium borides are similar to those of B-B bonds in solid α -B (2.00 Å, -3.49 eV), suggesting that Ir and B form covalent bonds. In addition, for the predicted Cm-Ir₄B₅ and Pmna-Ir₃B₄ compounds, the partial bonding states of B-B bonds shown in ICOHP are close to those in solid α -B (2.00 Å, -3.49 eV) and even larger than those in solid α -B (2.00 Å, -3.49 eV). In particular, in Cm-Ir₄B₅, it is also found that the shortest B-B pairs (1.89 Å) with the ICOHP value of -5.03 eV in graphene-like B sheet is only less than the ICOHP value of -7.72 eV in the smallest distance (1.67 Å) in α -B, which indicates that there is the strongest B-B covalent interaction. This conclusion also demonstrates the validity of the analyses of the Ir-B bond length, ELF, and Bader charge. In other words, the DOS, ELF, Bader charge analyses, and ICOHP all suggest that six phases possess Ir-B covalent bonds. In addition, there are strong B-B interactions in Cm-Ir₄B₅ and Pnma-Ir₃B₄.

4 Conclusions

In a word, the lowest energy (or ground state) and low energy metastable structures of various stoichiometric Ir–B compounds have been systematically studied based on particle swarm optimization combined with first-principles calculation. Besides the three known theoretical structures, C2/m-Ir₃B₂, Fmm2-Ir₄B₃, and Cm-Ir₄B₅, we predicted three low-energy metastable phases for each of the three compounds, namely, $P2_1/m$ -Ir₂B, $P2_1/m$ -IrB, and Pnma-Ir₃B₄, respectively. The obtained phonon spectra and elastic constants confirm that all the predicted $P2_1/m$ -Ir₂B, C2/m-Ir₃B₂, Fmm2-Ir₄B₃, $P2_1/m$ -IrB, Cm-

Ir₄B₅, and *Pnma*-Ir₃B₄ compounds are dynamically and mechanically stable. Six phases (except P2₁/m-IrB) have high bulk modulus and B/G ratio, making them promising low compressible material and toughness material. In particular, C2/m-Ir₃B₂ has the highest Vickers hardness of 13.1 and 19.4 GPa based on Chen's model and Mazhnik-Oganov's model, which is a potential hard material. According to the general anisotropy index and three-dimensional surface structure, the elastic anisotropy order of borides is $Ir_2B > IrB > Ir_4B_5 > Ir_3B_4 >$ Ir₄B₃ > Ir₃B₂. Additionally, the calculated electronic band structure and density of states show that all Ir-B crystals studied exhibit electronic characteristics of metals. Further analysis on the computed density of states, electron localized function, Bader charge analyses, and ICOHP indicate that strong Ir-B covalent bonds are present in P2₁/m-Ir₂B, C2/m-Ir₃B₂, P2₁/m-IrB, and Fmm2-Ir₄B₃, while there are complex combinations of strong B-B and Ir-B covalent bonds in Cm-Ir₄B₅ and Pnma-Ir₃B₄. We hope that this comprehensive structure search can promote further experimental on the iridium borides.

Author contributions

Jinquan Zhang: writing-original draft, visualization, formal analysis, software, investigation. Yuanyuan Jin: conceptualization, writing-review & editing, supervision, funding acquisition. Chuanzhao Zhang: conceptualization, software, writing-review & editing, data curation, supervision, funding acquisition. Yanqi Wang: validation, software. Libiao Tang: validation, software. Song Li: formal analysis, supervision. Meng Ju: funding acquisition, supervision. Jingjing Wang: software, supervision. Weiguo Sun: conceptualization, supervision. Xilong Dou: software, supervision.

Conflicts of interest

Authors declare no conflicts to interest.

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