

High-Pressure Synthesis of β -Ir₄B₅ and Determination of the Compressibility of Various Iridium Borides

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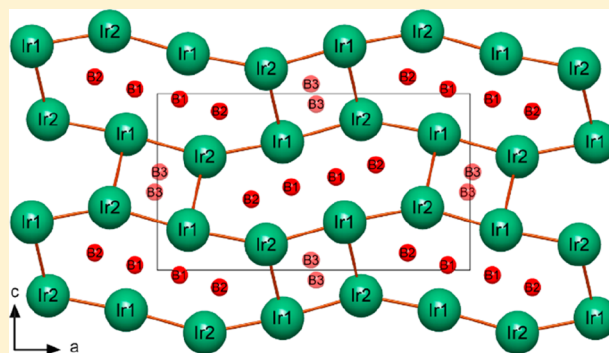
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Supporting Information

ABSTRACT: A new iridium boride, β -Ir₄B₅, was synthesized under high-pressure/high-temperature conditions of 10.5 GPa and 1500 °C in a multianvil press with a Walker-type module. The new modification β -Ir₄B₅ crystallizes in a new structure type in the orthorhombic space group *Pnma* (no. 62) with the lattice parameters $a = 10.772(2)$ Å, $b = 2.844(1)$ Å, and $c = 6.052(2)$ Å with $R1 = 0.0286$, $wR2 = 0.0642$ (all data), and $Z = 2$. The structure was determined by single-crystal X-ray and neutron powder diffraction on samples enriched in ¹¹B. The compound is built up by an alternating stacking of boron and iridium layers with the sequence ABA'B'. Additionally, microcalorimetry, hardness, and compressibility measurements of the binary iridium borides α -Ir₄B₅, β -Ir₄B₅, Ir₅B₄, hexagonal Ir₄B_{3-x} and orthorhombic Ir₄B_{3-x} were carried out and theoretical investigations based on density function theory (DFT) were employed to complement a comprehensive evaluation of structure–property relations. The incorporation of boron into the structures does not enhance the compressibility but leads to a significant reduction of the bulk moduli and elastic constants in comparison to elemental iridium.



INTRODUCTION

Over the past few years, metal borides attracted major interest within the scientific community, as many of them have outstanding physical properties, such as a high hardness (ReB₂, WB₄, FeB₄, IrB_{1.35}^{1–4}), extremely low compressibilities (ReB₂, OsB_{1.5}⁵), superconductivity (MgB₂, NbRuB_{6,7}), and outstanding high melting points (ZrB₂, HfB₂⁸). As a result of their high thermal stabilities, borides are often used in high temperature applications.⁹ Most borides can be synthesized at ambient pressure, which makes these materials interesting for industrial applications, as this synthesis route is relatively inexpensive and easily accessible.^{1,3,4,8–10}

In contrast to the limited experimental work on borides synthesized under high-pressure conditions, various theoretical studies predicted the possible synthesis of FeB₄, ReB₄, TaB₄, IrB₂, and IrB₄, among others, under high-pressure conditions.^{11–14} Specifically, the existence of a new iron-tetraboride FeB₄ with interesting physical properties like outstanding

hardness and superconductivity was originally predicted by Kolmogorov et al.¹⁵ and Bialon et al.,¹⁶ who suggested that FeB₄ could be synthesized under high-pressure conditions. In 2014, Gou et al. successfully synthesized FeB₄ under high-pressure conditions at a pressure of 15 GPa and a temperature of 1573 K.² Later on, the predicted orthorhombic structure as well as the superconductivity of FeB₄ were confirmed by experiment.^{2,15,16} In addition to FeB₄, only very few further borides such as, e.g., Fe₂B₇, MnB₄, Co₅B₁₆, and CrB₄ were synthesized under high-pressure conditions.^{2,17–24}

In order to expand the available limited data, the focus in this work is the synthesis of new iridium borides under high-pressure conditions. Up to now, already six binary iridium borides are known, namely, Ir₄B_{5+x} (formerly IrB_{1.35}),^{10,25–27} Ir₅B_{4+x} (formerly IrB_{1.1}),^{10,25,26} and the high and low

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temperature modification of $\text{Ir}_4\text{B}_{3-x}$ (formerly $\text{IrB}_{0.9}$).^{10,28} These phases were synthesized via high temperature syntheses by Aronsson et al.^{25,26} and by Rogl et al.²⁸ More recently, Zeiringer et al. reinvestigated the chemical compositions and structures of these iridium borides and suggested a slightly different labeling for a more suitable specification of the phase width.¹⁰ In 2016, Xie et al. successfully used a mechanochemical approach to synthesize two new iridium borides, namely, IrB_2 and IrB .²⁹ Rau et al. and Latini et al. investigated the hardness of $\text{Ir}_4\text{B}_{5+x}$ (formerly $\text{IrB}_{1.35}$) and $\text{Ir}_5\text{B}_{4+x}$ (formerly $\text{IrB}_{1.1}$) and discovered that very thin films of both phases show a high hardness of 49.8 at a load of 0.49 N for $\text{Ir}_4\text{B}_{5+x}$ and 43 GPa at 0.49 for $\text{Ir}_5\text{B}_{4+x}$.^{3,30} With the exception of the hardness of those phases, very little is known about other properties, such as compressibility, of the iridium borides. Numerous predictions of novel iridium borides with varying Ir:B ratio, which possibly could be synthesized under high-pressure/high-temperature conditions and are expected to show interesting mechanical properties, have been made.^{10,12–14,31–34}

In this context, our experiments led to the successful synthesis of a new modification of Ir_4B_5 which crystallizes in the centrosymmetric space group $Pnma$ in a new crystal structure type. Due to the extremely low scattering cross section of boron in comparison with iridium for X-rays, it is practically impossible to reliably determine the exact position and occupation of the boron atoms solely on the basis of X-ray diffraction data. Therefore, neutron powder diffraction data on ^{11}B -enriched samples were used in combination with X-ray diffraction methods to determine the structure. In addition to the synthesis of the new modification, we examined the compressibility, hardness, and thermodynamical properties of various other iridium borides.

■ EXPERIMENTAL SECTION

Synthesis. The starting materials iridium (99.9+%, ChemPur, Karlsruhe, Germany) and amorphous boron (99.9+%, ChemPur, Karlsruhe, Germany) or crystalline ^{11}B (99.9+% purity, 99.8+% enrichment, Ceradyne 3M, St. Paul, USA) were used for all phases. For the synthesis of $\beta\text{-Ir}_4\text{B}_5$, a stoichiometric Ir:B ratio of 1:3 was used. Experiments with a Ir:B ratio of 1:1.2 did not lead to the synthesis of $\beta\text{-Ir}_4\text{B}_5$ and showed that some excess of boron is necessary for the successful synthesis. The mixture was ground in a ball mill (Pulverisette 7-Premium Line, Fritsch, Idar-Oberstein, Germany) with an internal bowl volume of 80 mL for 100 min. Seven tungsten carbide balls were used as milling media with a ball to powder weight ratio of 1:15. Afterwards, the powder was inserted into a crucible made from hexagonal boron nitride (HeBoSint P100, Henze BNP GmbH, Kempten, Germany) and inserted into a 14/8 assembly. The sample was compressed to 10.5 GPa within 4.5 h by a high-pressure device consisting of a hydraulic 1000 t press (mavo press LPR 1000-400/50, Max Voggenreiter GmbH, Mainleus, Germany) and a Walker-type module (Max Voggenreiter GmbH) with eight tungsten carbide cubes (HA-7% Co, Hawedia, Marklkofen, Germany). The mixture was heated from ambient temperature to 1500 °C within 5 min. The temperature was held for 30 min and afterwards reduced to 700 °C in 1 h. After decompression, the sample was isolated from the surrounding assembly parts by mechanical separation. A more detailed description of this setup can be found in the literature.^{35,36}

Samples of $\alpha\text{-Ir}_4\text{B}_5$ were synthesized in an arc melter (MAM-1, E. Bühler GmbH, Hechingen, Germany) by annealing the elements in an Ir:B ratio of 1:1.5. The powders were mixed in an agate mortar and pressed into pellets of 5 mm diameter. Prior to the experiment, a titanium getter (99.95%) was molten to absorb any remaining traces of oxygen from the atmosphere in the reaction chamber. During the synthesis, the pellet was not molten but annealed by the plasma

several times from different sides. The temperature could thus not be determined exactly but must have been close to the melting point at the sample surface. A temperature gradient from the surface to the bulk must be assumed.

Samples of Ir_5B_4 could be synthesized in a custom-built tube furnace from the elements at 1223 K. The starting materials were mixed in an agate mortar in a Ir:B ratio of 1.25:1 and pressed into a dense pellet of 5 mm in diameter. The pellet was placed in a ceramic crucible and heated to 1223 K. The temperature was held for 24 h before switching the furnace off. The analysis of the powder X-ray diffraction pattern of Ir_5B_4 revealed that no side phases were present after the synthesis. The orthorhombic and hexagonal modifications of $\text{Ir}_4\text{B}_{3-x}$ were synthesized simultaneously from the same pellet. This was achieved by annealing the compacted powder with the plasma beam at low powers, which did not suffice to melt the elements. Since the phase transformation takes place at moderate temperatures (1373–1473 K), the temperature gradient from the surface to the bulk of the pellet in this method enabled us to obtain both modifications at once.

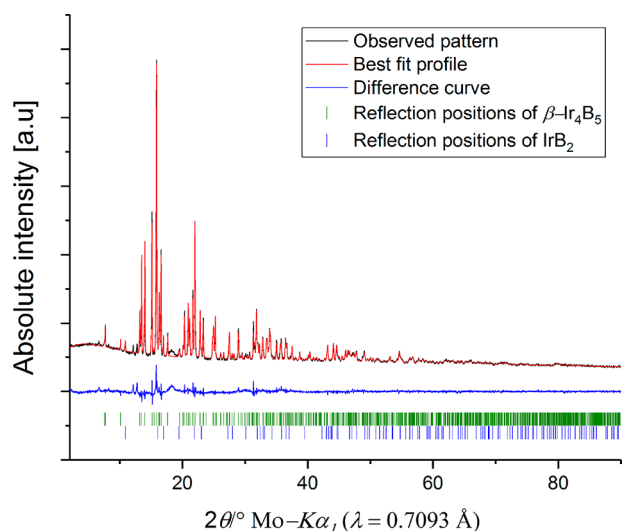
Crystal Structure Determination. The powder X-ray diffraction pattern of $\beta\text{-Ir}_4\text{B}_5$ was obtained in transmission geometry from a flat powder sample of the product. The measurements were carried out in transmission geometry using a STOE STADI P powder diffractometer equipped with $\text{Mo-K}_{\alpha 1}$ -radiation (Ge(111) monochromator $\lambda = 0.7093 \text{ \AA}$) in the 2θ range of $2.0\text{--}90.2^\circ$ with a step size of 0.015° . As a detector, a silicon microstrip solid state detector (Dectris Mythen 1K) was used. The lattice parameters shown in Table 1 were obtained through a Rietveld analysis of the powder pattern using the program TOPAS.³⁷ The Rietveld analysis of the powder pattern (Figure 1) revealed a very weak amorphous halo which can be explained by some unreacted amorphous boron, some weak reflections (e.g., at 10.9 , 16.9 , and 23.0°) which can be assigned to the compound IrB_2 (ReB_2 -type), and a few additional reflections (12.1 , 12.7 , and 18.2°) which could not yet be assigned to any known phase and presumably belong to an unknown minor impurity phase.

Small single-crystals of $\beta\text{-Ir}_4\text{B}_5$ were selected by mechanical fragmentation using a polarization microscope. A Bruker D8 Quest Kappa diffractometer with Mo-K_{α} radiation ($\lambda = 0.71073 \text{ \AA}$) was used to collect the single-crystal intensity data at room temperature. A multiscan absorption correction (SADABS-2014³⁸) was applied to the intensity data sets. The structure solution and parameter refinement (full matrix least squares against F^2) were performed by using the SHELX-13 suite with anisotropic displacement parameters for all atoms.^{39,40} To ensure that no symmetry operations were missing, the final solution was checked with PLATON.⁴¹ All relevant details of the data collection and the refinement are listed in Table 1, the positional parameters are listed in Table 2, and the important bond lengths are listed in Table 3. The program Diamond was used for the graphical representation (Figures 2–7) of the structure.⁴²

Neutron Powder Diffraction. Neutron powder diffraction was carried out at the neutron source FRM II at the Heinz Maier-Leibnitz Zentrum (MLZ), Garching, Germany, using the high-resolution neutron powder diffractometer SPODI with a Ge(551) monochromator ($\lambda = 1.5481 \text{ \AA}$). The data were collected in a range of 160° by a bank consisting of 80 ^3He detector tubes. A detailed description of the high-resolution neutron powder diffractometer can be found in the literature.^{43,44} Due to the high absorption cross sections of B and Ir, the samples were placed in a glass capillary with a diameter of only 1 mm for the measurement and measured for 90 min. The probe exhibits a packing density of around 2.39 g/cm^3 within the capillary. The packing density in combination with the atomic scattering factors of the used elements and the absorption leads to an attenuation factor for the sample of 2.546 cm^{-1} , which was used during the Rietveld refinement.^{45,46} The Rietveld refinement was carried out using the program TOPAS³⁷ and was used to determine the boron positions and occupancy. Due to the complicated synthesis process, the sample, which was used for the neutron diffraction, was relatively small and therefore the ratio of peak intensity to background was rather weak. The analysis of the neutron data, however, could unambiguously

Table 1. Crystal Data and Structure Refinement of β -Ir₄B₅ (Standard Deviations in Parentheses)

empirical formula	β -Ir ₄ B ₅
molar mass, g·mol ⁻¹	822.86
crystal system	orthorhombic
space group	<i>Pnma</i> (no. 62)
Powder Data	
powder diffractometer	STOE Stadi P
radiation	Mo-K α_1 (λ = 0.7093 Å)
<i>a</i> , Å	10.758(2)
<i>b</i> , Å	2.837(2)
<i>c</i> , Å	6.038(3)
<i>V</i> , Å ³	184.32(4)
Single-Crystal Data	
single-crystal diffractometer	Bruker D8 Quest Kappa
radiation	Mo-K α (λ = 0.71073 Å)
<i>a</i> , Å	10.772(2)
<i>b</i> , Å	2.844(1)
<i>c</i> , Å	6.052(2)
<i>V</i> , Å ³	185.47(2)
formula units per cell, <i>Z</i>	2
calculated density, g cm ⁻³	14.73
crystal size, mm ³	0.050 × 0.045 × 0.040
temperature, K	292(2)
absorption coefficient, mm ⁻¹	142.8
<i>F</i> (000)	666
θ range, deg	3.8–39.9
range in <i>hkl</i>	−19 ≤ <i>h</i> ≤ 19, −5 ≤ <i>k</i> ≤ 5, −9 ≤ <i>l</i> ≤ 10
total no. of reflections	7081
independent reflections	651
reflections with <i>I</i> ≥ 2 σ (<i>I</i>)	624
data/parameters	651/32
absorption correction	multiscan
goodness-of-fit on <i>F</i> ²	1.262
final <i>R</i> indices [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0271 <i>wR</i> 2 = 0.0635
final <i>R</i> indices (all data)	<i>R</i> 1 = 0.0286 <i>wR</i> 2 = 0.0642
largest diff. peak and hole, e Å ⁻³	5.07/−3.76

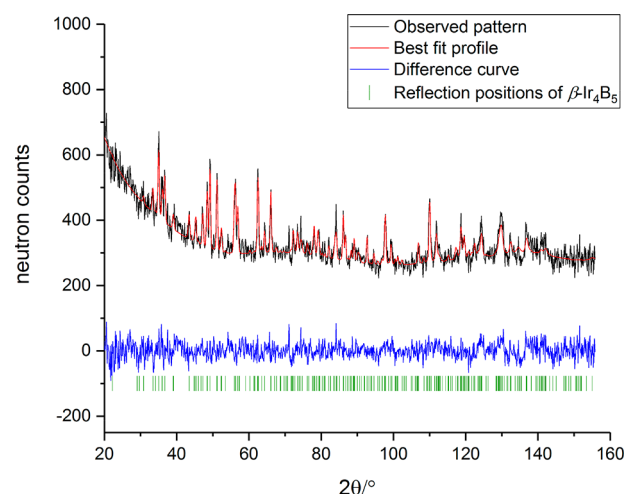
**Figure 1.** Rietveld plot of β -Ir₄B₅. The experimental powder diffraction pattern is shown in black, the calculated pattern is shown in red, and the difference plot is shown in blue. The reflection positions of β -Ir₄B₅ are shown in green, and those of IrB₂ in blue.**Table 2. Atomic Coordinates (Wyckoff Position 4c for All Atoms) and Equivalent Anisotropic Displacement Parameters *U*_{eq} (Å²) of β -Ir₄B₅^a**

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} ^b	s.o.f.
Ir1	0.59904(3)	1/4	0.2719(5)	0.0057(2)	1
Ir2	0.84838(3)	1/4	0.3555(5)	0.0055(2)	1
B1	0.5713(9)	3/4	0.528(2)	0.007(2)	1
B2	0.801(2)	3/4	0.097(2)	0.008(2)	1
B3	0.008(2)	1/4	0.557(3)	0.007(3)	0.5

^aData collected by single-crystal X-ray diffraction. ^b*U*_{eq} is defined as one-third of the trace of the orthogonalized *U*_{ij} tensor.

Table 3. Interatomic Distances (Å) in β -Ir₄B₅ (Space Group *Pnma*), Derived from Single-Crystal Data

2 × Ir1–B1	2.128(8)	Ir2–B1	2.16(2)
Ir1–B1	2.20(2)	2 × Ir2–B2	2.172(7)
Ir1–B2	2.25(2)	Ir2–B2	2.18(2)
Ir1–B3	2.22(2)	2 × Ir2–B3	2.17(2)
2 × Ir1–B3	2.25(2)	Ir2–B3	2.11(2)
2 × Ir1–Ir1	2.8445(2)	Ir2–Ir1	2.9489(4)
Ir1–Ir2	2.9489(4)	Ir2–Ir1	2.8082(5)
Ir1–Ir2	2.7332(5)	2 × Ir2–Ir2	2.8445(2)
Ir1–Ir2	2.8082(5)		
4 × B1–B2	2.02(2)	2 × B3–B3	1.59(2)
2 × B1–B1	2.12(2)		

**Figure 2.** Rietveld plot of β -Ir₄B₅ derived from the neutron data. The experimental powder diffraction pattern is shown in black, the calculated pattern is shown in red, and the difference plot is shown in blue.

verify the results of the X-ray structure determination (Figures 1 and 2, Supporting Information Tables S1 and S2).

Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, <http://www.fiz-karlsruhe.de/request>) on quoting the deposition number CSD-433663.

Determination of the Compressibility. For high-pressure experiments, Boehler-Almax-type diamond anvil cells were used.⁴⁷ The cells were loaded with Ne as a pressure-transmitting medium. Samples were placed in holes of 110–130 μm in diameter, which were drilled by a custom-built laser lathe in preindented Re gaskets (40–50 μm in thickness). The pressure was determined using the ruby fluorescence method.⁴⁸ Synchrotron X-ray diffraction experiments at high pressures were performed at the beamline P02.2 of the PETRA

III synchrotron (DESY, Hamburg, Germany). The diffraction patterns were acquired with a PerkinElmer XRD1621 detector at a wavelength of 0.2902 Å with beams focused to $1.5 \times 2.3 \mu\text{m}$ fwhm by Kirkpatrick–Baez mirrors. In order to improve the sampling statistics, samples were rotated by 20° during the 10 s data acquisition time. A CeO_2 standard was used to determine the sample-to-detector distance and for detector calibration during the experiments.⁴⁹ The diffraction patterns were corrected and integrated using the FIT2D and DIOPTAS software packages.^{50,51} The compressibilities were determined by investigating the dependence of the unit cell parameters upon compression which were obtained by Le Bail refinements. The data were fitted using a third-order Birch–Murnaghan (BM) equation of state^{52,53} using the EosFit software package.⁵⁴

Microcalorimetry. Microcalorimetry was performed using a Quantum Design thermal relaxation calorimeter (Physical Properties Measurement System, Quantum Design, San Diego, USA). Powdered samples of boron were thoroughly ground in a tungsten carbide mortar to reduce pores and encapsulated in a copper container (Alfa Aesar, 99.999%). In this case, the heat capacity of copper had to be subtracted afterward. Compacted, polycrystalline fragments of samples from $\alpha\text{-Ir}_4\text{B}_5$, $\beta\text{-Ir}_4\text{B}_5$, and iridium were prepared so that one flat and polished surface was present to guarantee a good thermal coupling of the sample to the sample holder. We have shown the accuracy of our measurements to be 1% in the temperature region between 40 and 300 K and 2% below 40 K by comparing the measurement of a standard material (Cu, Alfa Aesar, 99.999%) with the values obtained by Lashley et al.⁵⁵ The samples were mounted using Apiezon-N grease. All samples weighed between 10 and 25 mg and were measured in the temperature range between 1.8 and 395 K at 150 different temperatures. The temperature steps were reduced logarithmically from 395 to 1.8 K. At each step, the heat capacity was measured three times by the relaxation method using the two- τ model.^{55–57}

Hardness Measurements. Hardness measurements were carried out using a Vickers-type microhardness testing machine (HM-210A, Mitutoyo, Japan), equipped with an optical microscope and a 50 \times lens. A standard square-based diamond pyramid indenter with a 136° apex angle between the opposite faces was used for the indentation. Every indentation spot was generated by applying the following conditions: The loading and unloading times were kept at 5 s before and after the retention time of 15 s. The approaching speed of the indenter was $60 \mu\text{m/s}$. We created 10 indentations on the sample surface at each testing load (0.49, 0.98, 1.96, 2.94, 4.9, and 9.8 N). The Vickers hardness (H_V) was derived using the equation

$$H_V = \frac{1}{g} \frac{2F \sin \frac{136^\circ}{2}}{d^2}$$

with g being the standard gravitational acceleration (m/s^2), F the indentation load (N), and d the average diagonal imprint distance (mm). For the conversion to GPa, the results were multiplied by the factor 0.009807.

To provide an optimal specimen with a parallel surface for the hardness measurements, five polycrystalline fragments of $\beta\text{-Ir}_4\text{B}_5$ were embedded in a high-yield two-component epoxy (UHU Endfest 300, UHU, Brühl, Germany) inside a customized brass ring (5 mm in height, 20 mm in diameter). The entire setup was grounded using diamond coated polishing disks of varying mesh sizes, and the error in parallelism was $\pm 2 \mu\text{m}$. The top side, on which we carried out the measurements, was polished to a mirror-like finish using Al_2O_3 powder with grain sizes of 1 and $3 \mu\text{m}$.

Density Functional Theory. In order to obtain a better understanding of the structure–property relations of the synthesized compounds, we performed density functional theory (DFT) calculations employing the CASTEP⁵⁸ code. This code implements the Kohn–Sham DFT based on a plane wave basis set in conjunction with pseudopotentials. The plane wave basis set is unbiased (as it is not atom-centered) and does not suffer from basis set superposition errors in comparison to atom-centered analogues. It also makes

converged results straightforward to obtain in practice, as the convergence is controlled by a single adjustable parameter, the plane wave cutoff, which was set to 390 eV. All pseudopotentials were ultrasoft and were generated using the WC-GGA to allow for a fully consistent treatment of the core and valence electrons.⁵⁹ Brillouin zone integrals were performed by using Monkhorst–Pack grids with spacings of less than 0.028 \AA^{-1} between individual grid points. A simultaneous optimization of the unit cell parameters and internal coordinates was performed in the way that forces were converged to $<0.005 \text{ eV/\AA}$ and the stress residual was $<0.005 \text{ GPa}$. Elastic stiffness coefficients were derived by stress–strain calculations.

RESULTS AND DISCUSSION

Crystal Structure of $\beta\text{-Ir}_4\text{B}_5$. According to the systematic extinctions, the orthorhombic space group $Pnma$ (no. 62) was derived for $\beta\text{-Ir}_4\text{B}_5$. The dimensions of the unit cell are $a = 10.772(2) \text{ \AA}$, $b = 2.844(1) \text{ \AA}$, $c = 6.052(2) \text{ \AA}$, and $V = 185.47(2) \text{ \AA}^3$ (Table 1). The crystal structure was solved via single-crystal X-ray diffraction, but as it is difficult to reliably determine the occupancy and exact positions of the boron atoms solely on the basis of X-ray diffraction data, neutron powder diffraction was carried out afterward to verify the structure solution (Figures 1 and 2). Unless otherwise stated, the crystallographic details used in the following discussion (bond lengths and angles) are based on the excellent single-crystal X-ray data, as the quality of the powder pattern obtained from the neutron diffraction data was too low to deviate exact values from it (Figures 1 and 2, Tables 1 and S2). Nevertheless, the neutron diffraction data generally confirmed the single-crystal X-ray data. Furthermore, the investigations show that $\beta\text{-Ir}_4\text{B}_5$ possesses a phase width and could therefore be labeled as $\beta\text{-Ir}_4\text{B}_{5\pm x}$ as Zeiringer et al. also suggested for other iridium borides.¹⁰ However, in the following, we use the idealized formula $\beta\text{-Ir}_4\text{B}_5$. Figure 3 shows the structure, which

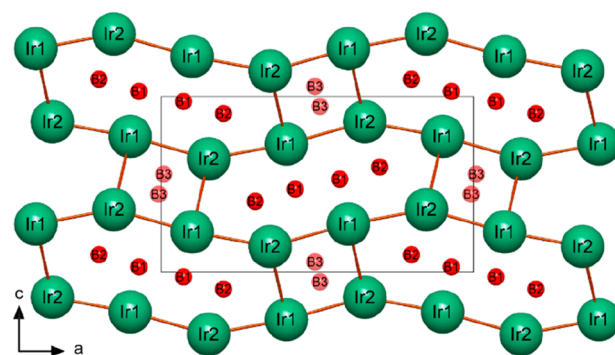


Figure 3. Stacking of alternating puckered boron (red) layers and puckered iridium atoms (light green).

can be described as stacking of alternating puckered boron layers (B, B') and puckered iridium layers (A, A') in the stacking sequence ABA'B' in the c direction of the crystal structure. The boron layers are built up by two parallel boron chains consisting of B1 and B2 atoms. These chains are interconnected via the B1 atoms of each chain, leading to the formation of a unique ribbonlike network of boron atoms (Figure 4). The boron–boron distances within the ribbons are $2.024(10) \text{ \AA}$ for B1–B1 and $2.122(14) \text{ \AA}$ for B1–B2 and are thus relatively long, but they correspond well to boron–boron distances in other transition-metal borides.^{10,17,25,60} These ribbons are located within large cavities formed by eight iridium atoms (Figure 3). Between the boron ribbons of each

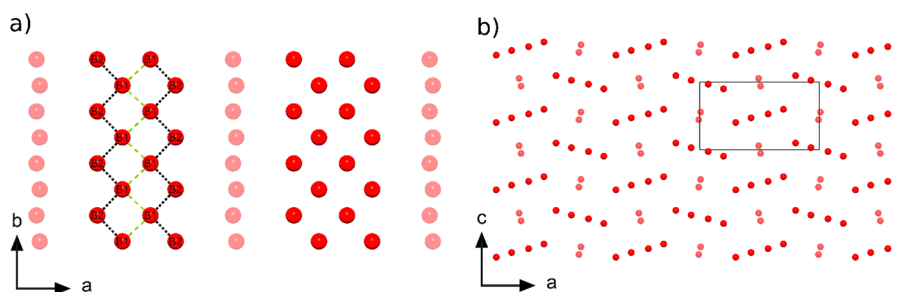


Figure 4. (a) Projection of a boron layer consisting of interconnected (green bonds) zigzag chains (black bonds) forming ribbons. Between the ribbons, half-occupied slightly bent boron chains (light red) are located. (b) Puckered boron layers along [010].

individual layer, iridium atoms form a column of face-sharing trigonal prisms that are partly centered by boron atoms B3. These prisms are connected via the square faces building up a column in the b direction (Figure 5). The structure

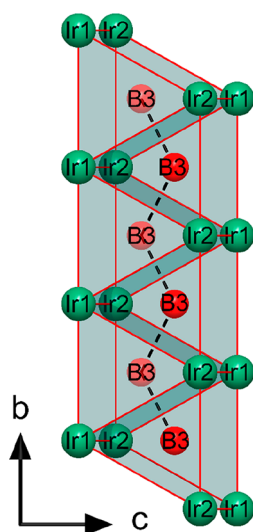


Figure 5. Column of face-sharing Ir_6 prisms centered by a half-occupied boron chain.

determination based on X-ray data revealed an occupancy of $\sim 50\%$ for B3 in the centers of the prisms within the column. The neutron data were used to verify the occupancy of around 50% for the B3 position and revealed a site occupancy factor of 55(4)%. The result of the neutron data is congruent with the

X-ray data and is reasonable regarding the fact that a full occupancy of the prisms would lead to the formation of a boron chain with a very short boron–boron distance of just 1.589(18) Å (Tables 2 and 3). As the B3 position exhibits an occupancy of marginally above 50%, some chain fragments with very short boron–boron distances may exist within the structure. The B3 positions are slightly shifted from being aligned in a perfectly straight chain (Figure 5). As the analysis of the X-ray data did not show any superstructure reflections, we cannot assume an ordering on the B3 site. The alignment within the individual boron layers (B and B') is identical, but the different layers are rotated and shifted with respect to each other (Figure 4b). The iridium atoms form a framework with two types of cavities, which are occupied by either the boron ribbons (B1 and B2) or the “chain” of isolated boron atoms (B3) (Figure 3). Iridium–iridium distances in the framework range from 2.7332(5) to 2.9489(4) Å, which is similar to the iridium–iridium distances in other borides and metallic iridium.^{10,26,28,61,62} Whereas the boron atoms B2 at the edge of the ribbons are coordinated by four iridium and two boron atoms, the boron atoms B1 have four close boron neighbors and four iridium atoms, leading to an 8-fold coordination (4 Ir + 4 B). The bond lengths of Ir–B within the iridium cage range from 2.128(8) to 2.249(11) Å and within the trigonal prism from 2.108(19) to 2.249(11) Å, which is slightly shorter than the sum (2.25 Å) of the covalent radii of the B atom ($r = 0.84$ Å) and the Ir atom ($r = 1.41$ Å). The iridium atoms are coordinated by six iridium atoms as well as by seven boron atoms, leading to a 13-fold coordination.

The closely related α -modification of $\text{Ir}_4\text{B}_{5+x}$ can be synthesized by arc melting and crystallizes in the monoclinic space group $C2/m$ with $a = 10.520(1)$ Å, $b = 2.895(1)$ Å, $c =$

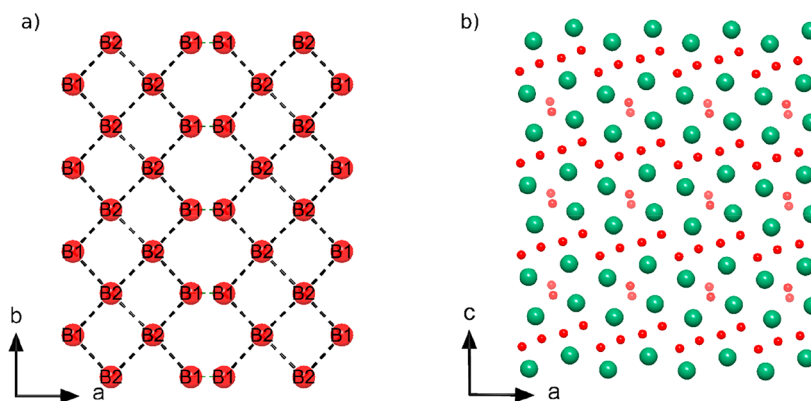


Figure 6. (a) Boron layer in $\alpha\text{-Ir}_4\text{B}_5$ viewed along $[00\bar{1}]$ exhibiting the boron network with shorter (green) and longer (black) boron–boron bonds. (b) Layered structure of $\alpha\text{-Ir}_4\text{B}_5$ consisting of boron layers and double iridium layers with boron atoms in the interstices.^{10,25,27}

6.095(1) Å, $\beta = 91.156(2)^\circ$, and $V = 185.6 \text{ Å}^3$.^{10,25,27,60} Just like $\beta\text{-Ir}_4\text{B}_5$, $\alpha\text{-Ir}_4\text{B}_5$ can also be described by a stacking of puckered boron and puckered double metal layers, however, without any displacements of the layers, therefore leading to the simple stacking sequence ABAB (Figure 6b). The interstices of the metal double layers are filled with boron atoms forming boron chains with rather short B–B distances of 1.61 Å. The boron atoms have a trigonal prismatic environment of iridium atoms, and the structure determination also revealed an occupancy of 50% for these boron positions.¹⁰ The same structural motif can be found in $\beta\text{-Ir}_4\text{B}_5$, but in contrast to the β -modification, these boron chains in the α -modification are located within the iridium layers and are not part of the boron layers (Figures 4, 6, and 7). Boron atoms with a trigonal

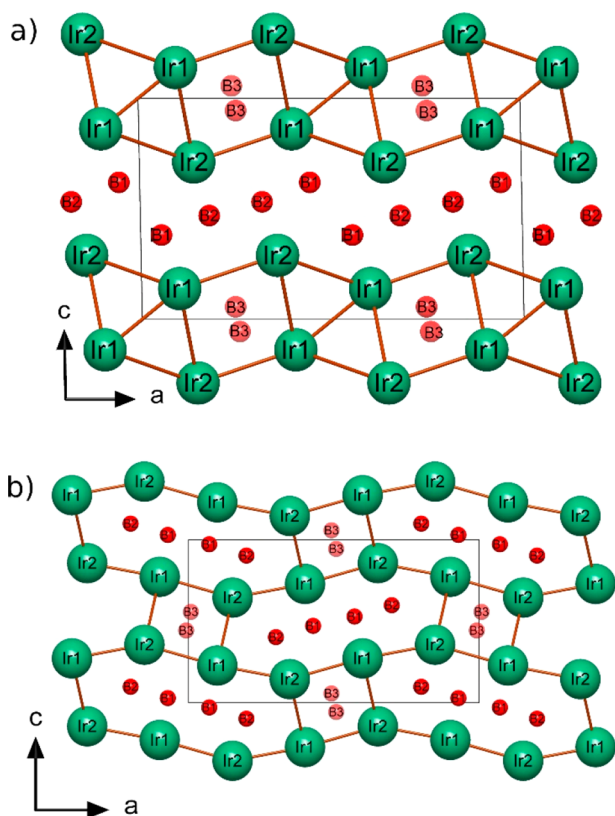


Figure 7. Structures of (a) $\alpha\text{-Ir}_4\text{B}_5$ and (b) $\beta\text{-Ir}_4\text{B}_5$.

prismatic metal environment are very common and can be found within several other transition metal borides such as Re_3B , Ni_7B_3 , and the members of the AlB_2 and CrB structure type family.^{63–66} In contrast to the arrangement of isolated boron ribbons in $\beta\text{-Ir}_4\text{B}_5$, the boron atoms within $\alpha\text{-Ir}_4\text{B}_5$ form an infinite boron network with B–B distances of 1.877 Å

between B1 and B1 and 2.106 Å between B2 and B2 (Figure 6).^{10,25–27,60}

Similar infinite two-dimensional boron networks can also be found within many other borides with a metal vs boron ratio ranging from MB_2 to M_2B_5 .^{27,61,65,67} The existence of interconnected and isolated boron chains within the same phase, as has been observed here in $\beta\text{-Ir}_4\text{B}_5$, has only been found in borides possessing the V_5B_6 -structure type. In V_5B_6 , the double chain consists of two antiparallel boron chains that are interconnected. The connection of the two chains leads to the formation of a boron network, which can also be described as a chain of aligned B_6 hexagons (Figure 8).^{68,69}

Compressibility. In the pressure regime up to 38 GPa, $\alpha\text{-Ir}_4\text{B}_5$ shows no structural phase transition. The bulk modulus is B_0 ($\alpha\text{-Ir}_4\text{B}_5$, third order) = 280(6) GPa with the pressure derivative B' ($\alpha\text{-Ir}_4\text{B}_5$, third order) = 4.4(4). The lattice parameters show a significant anisotropy in their individual compressibilities, with b being more compressible than the others. The higher compressibility along b can be rationalized by noting that this direction is parallel to the boron plane and the half-occupied boron chain is also oriented in this direction. The normalized unit cell parameters versus pressure are shown in Figure 9.

The β -modification of Ir_4B_5 was investigated up to a maximum pressure of 40 GPa, also showing no indication for a pressure induced structural phase transition (Figure 9b). The bulk modulus is 249(3) GPa for B_0 ($\beta\text{-Ir}_4\text{B}_5$, third order) with $B' = 3.2(3)$, which is smaller compared to the α -modification. The new modification $\beta\text{-Ir}_4\text{B}_5$, which was synthesized under high pressure conditions, shows a lower bulk modulus than $\alpha\text{-Ir}_4\text{B}_5$, which is in conflict with the expected behavior, namely, that high-pressure phases should form more dense structures and are harder to compress. Hence, $\beta\text{-Ir}_4\text{B}_5$ is not a high-pressure modification of $\alpha\text{-Ir}_4\text{B}_5$. High-pressure diffraction patterns of the two modifications at similar pressures are shown in Figures 10 and S1.

Ir_5B_4 was investigated up to a maximum pressure of 50 GPa, and there are no indications of a structural phase transition. The bulk modulus is B_0 (Ir_5B_4 , third order) = 310(5) GPa with the pressure derivative B' (Ir_5B_4 , third order) = 3.7(2). The lattice parameters do not show a significant anisotropy in their compression behavior (Figure S2).

We further investigated both modifications of $\text{Ir}_4\text{B}_{3-x}$ up to a maximum pressure of 33 GPa. We investigated a mixture of both modifications in one experiment in the same DAC at exactly the same pressure points. By scanning the sample with a high resolution ($2 \times 2 \text{ }\mu\text{m}^2$) grid, we found spots, where either orthorhombic $\text{Ir}_4\text{B}_{3-x}$ or hexagonal $\text{Ir}_4\text{B}_{3-x}$ were present as the main phase, along with unreacted iridium and the respective other polymorph. The bulk modulus of the orthorhombic modification from fitting a third-order BM

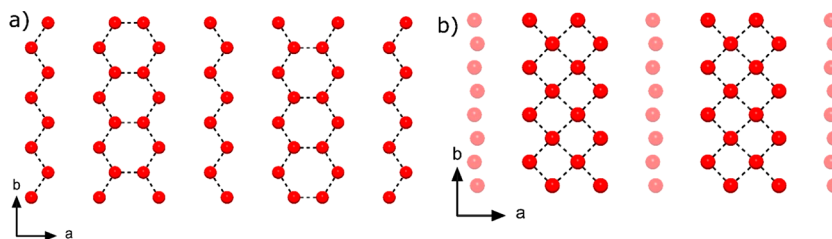


Figure 8. (a) Double and single boron zigzag chains in V_5B_6 .⁶⁸ (b) For comparison, double and single boron chains in $\beta\text{-Ir}_4\text{B}_5$.

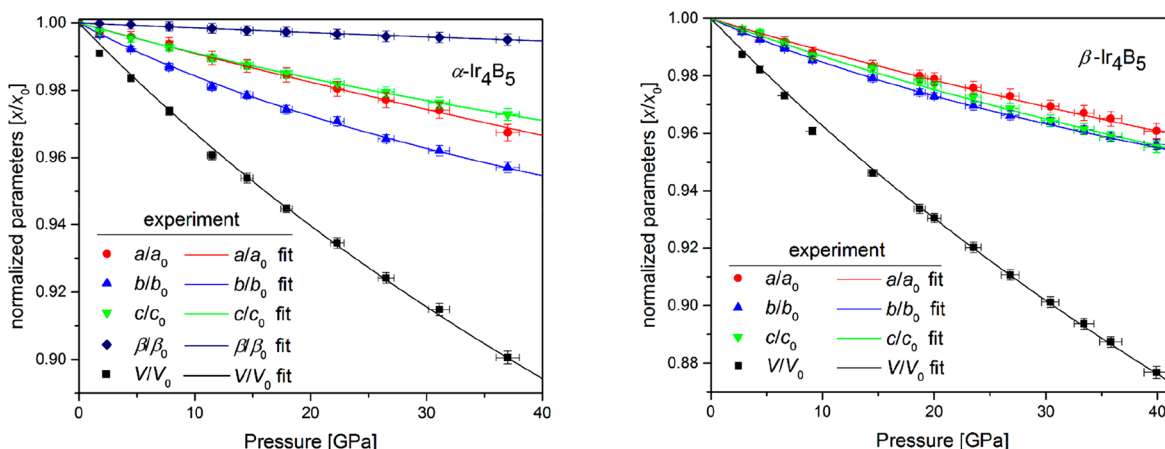


Figure 9. Compression behavior of the normalized unit cell parameters of α -Ir₄B₅ up to 38 GPa (left) and β -Ir₄B₅ up to 40 GPa (right).

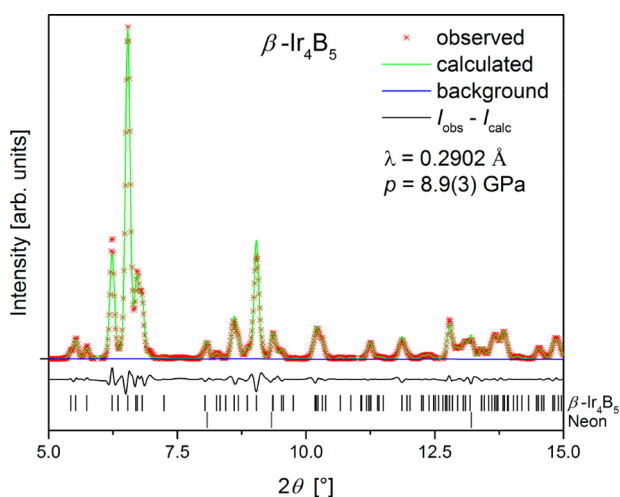


Figure 10. Le Bail refinement of β -Ir₄B₅ at 8.9(3) GPa. The experimental powder diffraction pattern is shown in red, the background is shown in blue, the calculated pattern is shown in green, and the difference plot is shown in black.

EOS is 320(6) GPa for B_0 (orthorhombic Ir₄B_{3-x} third order) with $B' = 5.2(4)$. The compression behavior of the lattice parameters shows no anisotropy. Hexagonal Ir₄B_{3-x} shows a higher compressibility with B_0 (hexagonal Ir₄B_{3-x} third order) = 279(4) GPa and $B' = 5.2(4)$ for the third-order fit. The compression behavior of the lattice parameters shows a slight anisotropy.

To obtain a better understanding of the changes introduced by the incorporation of boron into the structures, we collected pressure data of elemental iridium up to a pressure of 50 GPa. We found a bulk modulus of B_0 (Ir, third order) = 326(3) GPa with $B' = 5.3(2)$. A summary of the compressibilities of all phases is given in Table 4. The compression behavior showing the third-order fits is displayed in Figures 9 and S2–S5, and the pressure dependence of the unit cell parameters is listed in Tables S2–S6.

The incorporation of boron into the structures does not enhance the incompressibility but leads to a significant reduction of the bulk modulus in comparison to elemental iridium. This is in contrast to the observations on rhenium or osmium borides, where the incorporation of boron leads to a decrease of the compressibility with respect to the compressibility of the elements.^{5,70–72} The investigated phases however

Table 4. Experimental and Calculated Results of the Compressibility^a

compound	space group	BM order	B_0 (GPa) (exp)	B'
α -Ir ₄ B ₅	C2/m	2 nd	292(5)	4
		3 rd	280(6)	4.4(3)
		DFT	225(1)	
β -Ir ₄ B ₅	Pnma	2 nd	239(3)	4
		3 rd	249(3)	3.2(3)
		DFT	265(1)	
Ir ₅ B ₄	I4 ₁ /a	2 nd	304(6)	4
		3 rd	310(5)	3.7(2)
		DFT	287(1)	
orthorhombic Ir ₄ B _{3-x}	Cmc2 ₁	2 nd	336(8)	4
		3 rd	320(6)	5.5(4)
		DFT	<i>b</i>	
hexagonal Ir ₄ B _{3-x}	P6m2	2 nd	293(4)	4
		3 rd	279(4)	5.2(4)
		DFT	<i>b</i>	
Ir	Fm3m	2 nd	341(5)	4
		3 rd	326(3)	5.3(2)
		DFT	346(1)	

^aThe DFT values were obtained from stress–strain relations. ^bDue to the partial occupation of some boron positions in the orthorhombic and hexagonal Ir₄B_{3-x} phases, no appropriate model calculation could be carried out.

follow the trend to become more compressible as the amount of boron in the structures increases. Orthorhombic Ir₄B_{3-x} being the most metal-rich phase, almost reaches the bulk modulus of elemental iridium. The new phase β -Ir₄B₅ on the other hand shows a compressibility which is approaching the rather low value of 224(15) GPa of elemental boron.⁷³ The findings in this study thus support the statement of Gu et al., who correlated an increasing amount of boron in borides with a decreasing bulk modulus.⁵

Hardness. The hardness of β -Ir₄B₅ was obtained at different indentation loads in order to allow an extrapolation of the load dependence and in order to enable a comparison to data from earlier studies. The asymptotic response of the material's hardness to increasing loads is depicted in Figure 11. In the load regime between 9.8 and 2.94 N, the hardness remains almost constant, showing a hardness of approximately 16 GPa. At lower forces, the hardness increases to a maximum value of H_V (0.49 N, β -Ir₄B₅) = 22.6(2.8) GPa at 0.49 N. The

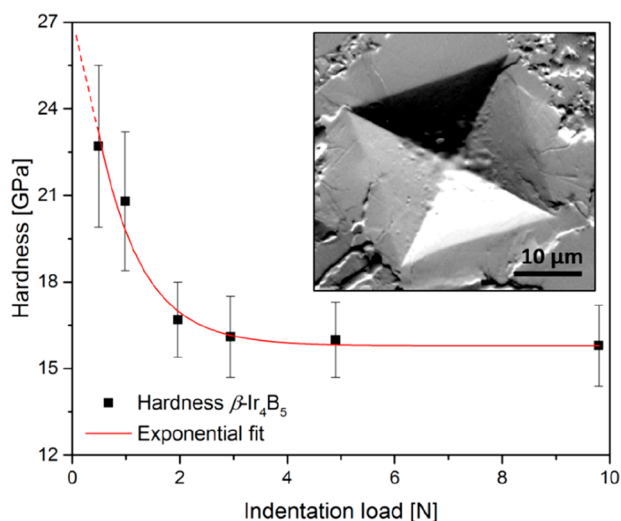


Figure 11. Load-dependent hardness of β - Ir_4B_5 . The data were fitted with an exponential to extrapolate the material hardness at infinitesimal loads. The extrapolation of the fit is indicated by a dashed line.

hardness of β - Ir_4B_5 , which ranges from H_V (9.8 N, β - Ir_4B_5) = 15.8(1.2) GPa to H_V (0.49 N, β - Ir_4B_5) = 22.6(2.8) GPa, is significantly lower than the values reported for the α -modification (49.8 at 0.49 N and 18.2 GPa at 9.8 N), or Ir_5B_4 (43 GPa).^{3,30} However, the hardness data for α - Ir_4B_5 and Ir_5B_4 were obtained using very thin films consisting of nm-sized crystals on a substrate of different chemical constitution (TiB_2/BN composite) which might have resulted in significant overestimation of the values. Furthermore, the XRD pattern of Ir_5B_4 in the study of Latini et al. (2010) showed indications of an impurity phase which formed during the laser deposition experiments. In contrast, our results are in good agreement with the observation of Samsonov et al. on bulk samples, who found a hardness of only 15.8(8) GPa for Ir_5B_4 .⁷⁴ Therefore, we conclude that the bulk hardness of iridium boride phases is not as high as previously assumed on the basis of thin film measurements.

Microcalorimetry. Microcalorimetry was performed on polycrystalline samples of α - Ir_4B_5 and β - Ir_4B_5 , which weighed between 20 and 25 mg. The comparison of the heat capacity curves for both modifications can be seen in Figure S6. Both curves show no peaks at low temperatures, and hence, there seems to be no transition into a superconducting state down to 2 K. There is excellent agreement for the ambient temperature values of the heat capacity, enthalpy, and entropy with published data for elemental boron and iridium. The Debye temperature of β - Ir_4B_5 (444(4) K) is higher than the temperature of α - Ir_4B_5 (392(4) K), whereas both are in the same temperature range as elemental iridium (420 K) and

noticeably smaller than the Debye temperature of elemental boron (1219 K). The herein determined values for the Debye temperature of elemental iridium (343(3) K) and boron (928(9) K) are smaller than the values tabulated in the literature.^{75,76} These deviations can arise from different fitting ranges and fitting difficulties. The T^3 -plots are shown in Figures S7–S10. All derived thermodynamic values, including those of elemental boron and iridium, are listed in Table 5.

DFT Calculations. DFT calculations were performed on simplified model structures. We disregarded occupational disorder in the structures and assumed full site occupancies for each phase. These simplifications turned out to be inappropriate for both $\text{Ir}_4\text{B}_{3-x}$ modifications, and therefore, no further calculations were carried out for this composition. Ir_5B_4 was approximated by $\text{Ir}_{20}\text{B}_{16}$, α - Ir_4B_5 by $\text{C2}/m$ - Ir_8B_{12} with a full occupation of the Wyckoff position 4i, and β - Ir_4B_5 by Pnma - Ir_8B_{12} . Stress–strain calculations allowed us to obtain the elastic stiffness coefficients c_{ij} , bulk modulus B , shear modulus G , Young's modulus Y , Poisson's ratio ν , Debye temperature Θ_D , universal anisotropy index A_U , and hardness H (Table 6). The calculated Debye temperatures for α - Ir_4B_5

Table 6. Elastic Properties from the Elastic DFT-GGA Calculations

	$\text{C2}/m$ - " Ir_8B_{12} "	Pnma - " Ir_8B_{12} "	" $\text{Ir}_{20}\text{B}_{16}$ "	
	α - Ir_4B_5	β - Ir_4B_5	Ir_5B_4	Ir
c_{11} (GPa)	373(3)	482(4)	494(2)	583(1)
c_{22} (GPa)	303(3)	390(1)		
c_{33} (GPa)	303(2)	433(4)	460(2)	
c_{44} (GPa)	50(1)	112(1)	72(1)	256(1)
c_{55} (GPa)	125(1)	102(2)		
c_{66} (GPa)	58(1)	60(1)	162(1)	
c_{12} (GPa)	150(2)	170(2)	221(2)	228(1)
c_{13} (GPa)	160(2)	122(2)	177(1)	
c_{15} (GPa)	58(1)			
c_{16} (GPa)			40(1)	
c_{23} (GPa)	217(2)	250(2)		
c_{25} (GPa)	−32(1)			
c_{35} (GPa)	7(1)			
c_{46} (GPa)	−29(1)			
B_{cij} (GPa)	225(1)	265(1)	287(1)	346(1)
G_{cij}^a (GPa)	63(8)	99(5)	110(6)	222(2)
Y_{cij} (GPa)	180(10)	266(10)	295(15)	550(5)
ν_{cij}	0.37(1)	0.33(1)	0.33(1)	0.23
Θ_D (K)	324(2)	414(2)	382(2)	428(3)
A_U^b	2.5(1)	0.7	0.9(1)	0.16(1)
H (GPa)	4.5(5)	8.5(5)	9(1)	25(1)

^a $2G(1 + \nu) = Y = 3B(1 - 2\nu)$ for isotropic materials. ^b $A_U = 5G^V/G^R + B^V/B^R - 6 \geq 0$ (G^V and G^R Voigt and Reuss estimates of G , B^V and B^R = Voigt and Reuss estimates of B).⁷⁷

Table 5. Thermodynamical Properties of α - Ir_4B_5 , β - Ir_4B_5 , Elemental Ir, and Elemental B at 298 K

compound	C_p (J/mol K)	H_{298}^0 (J/mol)	S_{298}^0 (J/mol K)	Θ_D (K)	reference
α - Ir_4B_5	291(1)	39770(700)	227(2)	392(4)	this study
β - Ir_4B_5	223(1)	32930(600)	191(1)	444(4)	this study
Ir elemental	24.8(2)	5232(50)	35.3(3)	343(3)	this study
Ir elemental	25.09	5266	35.49	420	Arblaster ⁷⁶
B elemental	11.2(1)	1220(15)	5.93(9)	928(9)	this study
B elemental	11.1(1)	1222(8)	5.90(8)	1219	Thompson and McDonald ⁷⁵

(324(2) K) and β -Ir₄B₅ (414(2) K) are in moderate agreement with the experimental values (392(4) K for α -Ir₄B₅ and 444(4) K for β -Ir₄B₅). The Debye temperature for elemental iridium (428(3) K) is in excellent agreement with the value from the literature (420 K).⁷⁶ The calculated bulk moduli of the three phases are similar to the values obtained by the experimental measurements (Table 4). This justifies to some extent the neglect of the partial occupation but, conversely, also indicates that a minor change in the boron content will not influence the physical properties significantly. The values of the calculated and measured hardness however differ considerably for the phases. These deviations can be explained by the fact that the hardness of a material is primarily a surface property and the calculations are volume-based parameters.

CONCLUSIONS

We report the successful synthesis of β -Ir₄B₅, the first 5d transition metal boride synthesized under high-pressure conditions, as well as the synthesis and characterization of the binary iridium borides orthorhombic Ir₄B_{3-*x*}, hexagonal Ir₄B_{3-*x*}, Ir₅B₄, and α -Ir₄B₅. The structure of the new modification was solved unambiguously by combining single-crystal XRD and complementing neutron diffraction experiments to unequivocally locate the boron atoms and determine their site occupancies. There are some similarities between the structures of β -Ir₄B₅ with both α -Ir₄B₅ and the V₃B₆-structure type; however, the alignment of the double boron chains in combination with the half-occupied single chain in β -Ir₄B₅ is unique and therefore constitutes a new structure type. Even though the synthesis of β -Ir₄B₅ was carried out under high-pressure/high-temperature conditions, our findings (compressibility, unit cell volume, microcalorimetry) clearly show that it is not a high-pressure polymorph of Ir₄B₅. The structure was not among the numerous predicted possible structures. By using microcalorimetry measurements, the heat capacities of α -Ir₄B₅ and β -Ir₄B₅ were determined. Both phases do not seem to become superconducting at low temperatures. The hardness measurements revealed a significantly lower hardness for bulk β -Ir₄B₅ than Latini et al. found for thin films of α -Ir₄B₅.³⁰ As the crystal structure and composition for both modifications are similar, the huge difference in the hardness value presumably arises from other reasons. We conclude that the hardness of α -Ir₄B₅ is either not as high as previously assumed on the basis of thin films measurements or that such observations are at least not extendable to bulk properties. The values for the bulk moduli B_0 of the iridium borides vary between 249(3) and 320(6) GPa (third-order BM fits). Iridium borides do not reach the ultra-incompressibility of diamond (443 GPa) and OsB (431–453 GPa), or other incompressible period-6 transition metal borides.^{5,71} The incorporation of boron into the structures does not enhance the compressibility but leads to a significant reduction of the bulk modulus in comparison to elemental iridium (B_0 , third order = 326(3) GPa). These findings for iridium borides are in contrast to the observations on rhenium or osmium borides, where the incorporation of boron leads to a decrease of the compressibility with respect to the compressibility of the elements.^{5,70–72} Thus, ongoing research in the field of binary borides is crucial for a better understanding of the exact influence of boron incorporation into heavy transition metals.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b01541.

Detailed description of the derivation for the compressibility and microcalorimetry, crystallographic data collected by neutron and X-ray diffraction, X-ray powder pattern of β - and α -Ir₄B₅ at 7.8(3) GPa, compression behavior of β -Ir₄B₅, α -Ir₄B₅, Ir₅B₄, orthorhombic Ir₄B_{3-*x*}, and hexagonal Ir₄B_{3-*x*}, heat capacity of α -Ir₄B₅ and β -Ir₄B₅, and Debye temperature of α -Ir₄B₅, β -Ir₄B₅, elemental iridium, and elemental boron (PDF)

Accession Codes

CCDC 1847116 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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All authors have given approval to the final version of the manuscript

Notes

The authors declare no competing financial interest.

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