

Hardening in Tungsten Tetraboride with the Addition of Carbon, Zirconium, and Silicon: Intrinsic vs Extrinsic Effects

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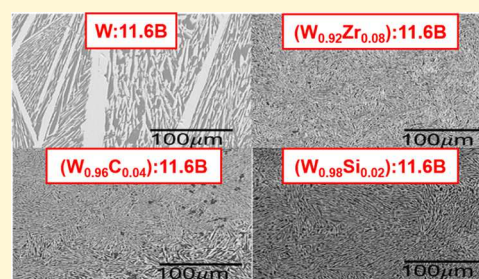


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ABSTRACT: Alloys of tungsten tetraboride (WB_4) with the addition of C and Si were prepared by arc-melting of the constituent elements. The phase purity was established by powder X-ray diffraction (PXRD) and surface morphology by scanning electron microscopy (SEM) analysis. Vickers hardness measurements showed hardness enhancement for alloys with a nominal composition of $(W_{0.98}Si_{0.02}):11.6B$ and $(W_{0.95}C_{0.05}):11.6B$ of 52.2 ± 3.0 and 50.5 ± 2.5 GPa, respectively, compared to 41.2 ± 1.4 GPa for pure WB_4 . $(W_{0.92}Zr_{0.08}):11.6B$ was determined in previous work to have a hardness of 55.9 ± 2.8 GPa. Bulk moduli were calculated following analysis of high-pressure radial diffraction data and were determined to be 329 ± 4 ($K' = 2$) and 390 ± 9 ($K' = 0.6$) GPa for 8 atom % Zr and 5 atom % C-doping, respectively, compared to 326–339 GPa for pure WB_4 . Computational analysis was used to determine the dopant positions in the crystal structure, and it was found that Zr primarily substitutes W in the 2c position, Si substitutes for the entire $B3$ trimers, and C inserts in the B_{hex} -layer. The hardness enhancement in the case of Zr-doping is attributed primarily to extrinsic hardness effects (nanograin morphology), in the case of C—to intrinsic effects (interlayer bond strengthening), and in the intermediate case of Si—to both intrinsic and extrinsic effects (bond strengthening and fine surface morphology).



INTRODUCTION

Transition metal borides possess a large variety of crystal structures,¹ which results in the ability to tune many useful material characteristics, including their electronic, magnetic, optical, thermal, and mechanical properties.^{1–7} The most commonly used mechanical property is hardness, and, as a consequence, superhard materials (possessing a Vickers hardness of greater than 40 GPa) and ultracompressible materials (possessing a bulk modulus greater than 300 GPa) have become increasingly popular subjects for research.^{8–11}

Diamond, the hardest naturally occurring material, is expensive and cannot be readily used in the processing of iron-containing alloys due to the formation of iron carbide. Cubic boron nitride, the second hardest material, requires high pressure and high temperature to synthesize its hard polymorph. Boron carbide, the third hardest material, has a disadvantage similar to that of diamond in the cutting of iron as well as an expensive manufacturing process. Transition metal borides are thus interesting alternatives as more cost-effective and easily synthesizable superhard materials.

In the past decade, the field of metal borides has seen a host of phases, their alloys, and solid solutions: ReB_2 (the first reported superhard metal boride),^{8,9} $W_{1-x}Ta_xB$ (having an enhanced bulk modulus compared to WB),^{11,12} tungsten tetraboride (providing a cost-effective alternative to

ReB_2),^{13–18} metal dodecaborides (MB_{12})^{19–22} (possessing true three-dimensional (3D) networks of boron atoms), and ternary metal borides (featuring complex atomic arrangements).²³ The hardness of these metal borides can be enhanced through both intrinsic and extrinsic hardening effects. Intrinsic hardness generally involves solid-solution formation and novel chemical bonding effects, while extrinsic hardness is governed by surface grain hardening (Hall-Petch), patterning, and nanosize effects.²⁴

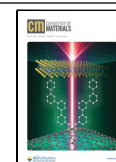
WB_4 is an incongruently melting phase traditionally synthesized with excess boron ($W/B \approx 1:12$), as this suppresses the formation of the softer tungsten diboride (WB_2 , $P6_3/mmc$). However, the formation of WB_4 through the use of excess boron is accompanied by crystalline β -rhombohedral boron ($R\bar{3}m$).^{10,14,25} Due to the presence of the two phases (WB_4 and β -rhombohedral boron), it is possible to control the size and shape of the grains and as a result influence bulk mechanical properties through extrinsic

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effects.^{14,17} Alternatively, by substituting some of the tungsten atoms with tantalum, it is possible to stabilize the WB₄ structure at near-stoichiometric amounts of boron, with a nominal composition of (W_{0.67}Ta_{0.33}):4.5B.¹⁸

Tungsten tetraboride (WB₄, *P6₃/mmc*) has a unique structure among borides that contains partially filled metal and boron sites as well as voids (Figure 1). This defect

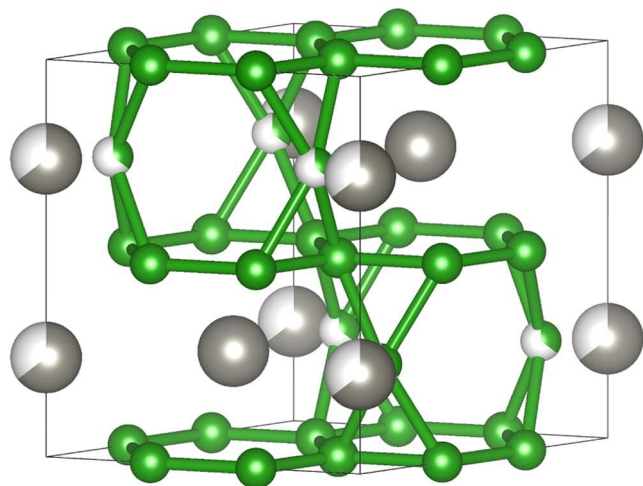


Figure 1. Crystal structure of WB₄ with the *P6₃/mmc* space group (ICSD, Inorganic Crystal Structure Database –291124).⁵¹ Tungsten atoms are shown in gray, while boron atoms are shown in green; partially occupied positions are depicted by half-filled atoms. Adapted with permission from ref 31. Copyright 2021 American Chemical Society.

structure enables WB₄ to host both substitutional and interstitial dopants in voids and partial occupancy sites.^{13–15,17} The addition of dopants leads to an enhancement of the hardness. The hardening appears to be intrinsic in the case of Ta, Mo, Ti, and Hf,^{13–15} and some combination of intrinsic and extrinsic effects in the case of Zr, Y, Sc, and some lanthanides.^{14,17}

In this study, we investigated the effects of adding carbon and silicon on the mechanical properties of WB₄. It was found that both elements have a similar effect on surface morphology to the addition of zirconium studied previously.¹⁴ Tungsten tetraboride (WB₄) has a pseudo-cage structure that consists of alternating hexagonal layers of boron and tungsten with some partially occupied tungsten sites. Boron trimers sitting at those unoccupied sites combine with the boron layers to form “hourglass” structures; when the boron trimers above and below the boron layer correlate, they form distorted cuboctahedral cages. Therefore, WB₄ is able to accommodate dopants by either substitutional or interstitial doping into the partially filled metal and boron sites or into the voids. The defect structure allows the hardness of WB₄ to be tuned by doping with other transition metals, such as tantalum (Ta), manganese (Mn), and chromium (Cr).¹⁶ However, little is known about the dopant positions in the WB₄ cage structure. Our goal here is to use a combination of high-pressure studies and computational chemistry to understand the mechanisms for enhanced hardness upon doping WB₄ with boron-like light elements (C and Si) as well as with transition metals (Zr) and whether the enhancement is intrinsic or extrinsic (or some combination of both) in nature.

RESULTS AND DISCUSSION

Figures S1A,B and 2 show the powder X-ray diffraction data for alloys with nominal compositions of (W_{1–x}C_x):4.5B, (W_{1–x}Si_x):4.5B, (W_{1–x}Zr_x):4.5B, (W_{1–x}C_x):11.6B, and (W_{1–x}Si_x):11.6B. For the first three cases, the main WB₄ phase is accompanied by the lower boride phase (WB₂) at all concentrations of carbon, silicon, and zirconium addition. This can be explained by the fact that at a 1:4.5 metal-to-boron ratio, the liquid peritectically decomposes into WB₄ and WB₂ upon cooling.^{18,25,26} This further suggests that neither carbon nor silicon stabilize the WB₄ phase without the formation of the lower boride, which suggests that they do not substitute for tungsten in the structure, being nonmetals by nature. For the case with Zr, ZrB₂ phase is present at concentrations of 17 atom % Zr and above. While presence of zirconium does not suppress the formation of WB₂ at 4.5B, it can be explained by the fact that some of Zr is incorporated into the WB₄ cage voids (similar to the case of (W_{1–x}Zr_x):11.6B),¹⁴ while the excess is used to form ZrB₂ and a solid solution with WB₂ (they adopt similar layered structures and it is possible to stabilize WB₂ in the ZrB₂ (AlB₂) structure).

For the last two cases, the main WB₄ phase is present, while the lower boride is absent due to the stoichiometry used. At a metal-to-boron ratio of 1:11.6, the liquid peritectically decomposes upon cooling to form WB₄ and crystalline β -rhombohedral boron.^{26–28} Despite the presence of some crystalline β -rhombohedral boron, it is not seen in the X-ray diffraction (XRD) patterns (Figure 2) due to its significantly lower intensity when compared to the WB₄ and WB₂ phases. For both carbon and silicon at high concentrations, the powder diffraction data indicates the formation of insoluble impurities, suggesting a clear solubility limit.^{13–15,17,18} Secondary phases can be seen in all four cases at high addition fractions and more prominently in the case of added carbon, where with increasing concentration, peaks corresponding to boron carbide can be seen. This is further corroborated by the changes in lattice parameters *a* and *c* for the alloys of WB₄ with carbon and silicon prepared at 1:4.5 and 1:11.6 metal-to-boron ratios (Figure 3). The lattice parameters do not change dramatically with the increasing concentration of carbon and silicon, from which we can deduce that neither of these elements substitutes for tungsten in any significant amounts. They can, however, substitute for the partially occupied boron atoms in the WB₄ structure.²⁸

To identify the preferred positions of Zr, C, and Si impurities and corroborate the experimental observations, we used density functional theory (DFT) calculations. First, we computationally identified the most stable realization of WB_{4.2} with respect to the B₃-trimer distribution. Next, that structure was used to compute the placement and formation enthalpies of the doped materials.

The WB_{4.2} unit cell structure with *P6₃/mmc* symmetry was taken as the foundation for the calculations.²⁸ However, it was shown by Lech et al. that the crystal structure of WB_{4.2} is disordered with a $\sim 2/3$ chance of a B₃-trimer substituting a W atom in the Wyckoff 2(b) position. Therefore, to account for fractional occupancy sites, a $3 \times 2 \times 1$ supercell was chosen, since it is the smallest supercell that guarantees an integer number four B of B₃-trimers in the structure. Within this supercell, a set of structures was sampled, including but not limited to structures of high symmetry, high bulk modulus, low energy, etc. (Figure S1A). The structure shown in Figure 4 is

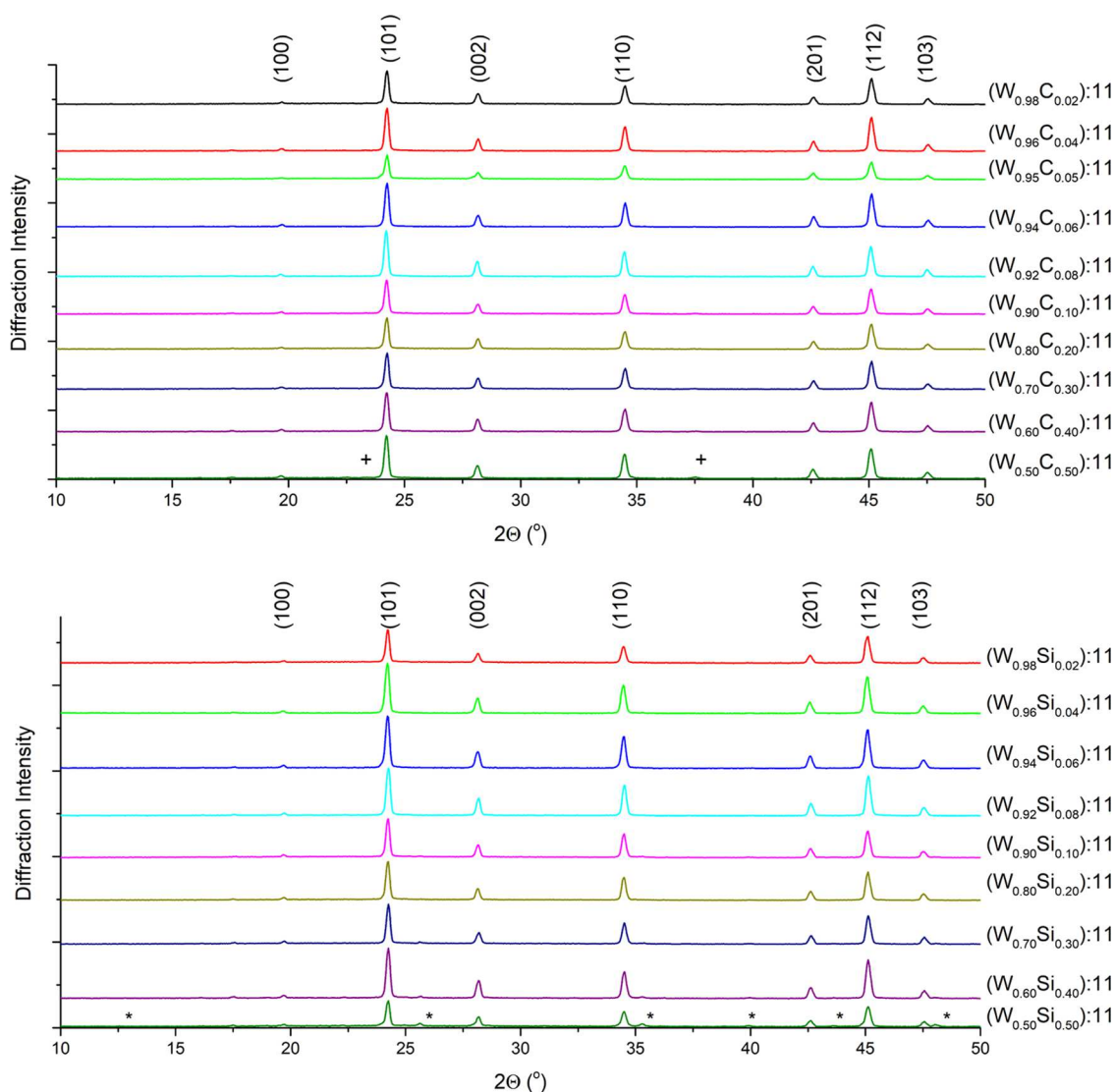


Figure 2. Powder XRD patterns (10–50° 2 θ) of alloys of nominal composition (top) ($W_{1-x}C_x$):11.6B and (bottom) ($W_{1-x}Si_x$):11.6B. WB_4 ($P6_3/mmc$, JCPDS 00–019–1373) is present at all concentrations of C and Si. Peaks corresponding to a boron carbide phase (denoted by +) and $R\bar{3}m$, JCPDS 00–035–0798) can be observed at heavy concentrations of carbon addition. Peaks corresponding to WB_2 (denoted by *), ($P6_3/mmc$, JCPDS 01–073–1244)) can be observed at heavy concentrations of silicon addition. Spectra for ($W_{1-x}Zr_x$):11.6B is discussed in ref 14.

the one on which we focus the discussion, as it is the structure with not only the highest symmetry, $Cmcm$, but also the highest calculated bulk modulus ($B_0 = \sim 293$ GPa). Furthermore, the $Cmcm$ structure was found to be the most stable at finite temperature with inclusion of configurational entropy.⁴³

To identify the preferred positions of C, Si, and Zr in the structure shown in Figure 4, the formation enthalpies, H_0 , were calculated (Table 1). By this metric, the preferential position for C is in the B_{hex} -layer in the [001] plane, in agreement with the hypothesis derived from the experiment. Si preferentially substitutes for the entire B_3 -trimer. Zr substitutes W in the Wyckoff 2(c) position (next to the edge of the B_3 -trimer), and there is only a slightly less preferred structure where Zr substitutes for W in the Wyckoff 2(c) position (next to the vertex of the B_3 -trimer). Indeed, *ab initio* DFT calculations support experimental findings regarding the location of impurities within $WB_{4.2}$.

The DFT calculations make it clear that C, Si, and Zr can substitute into the $WB_{4.2}$ lattice, resulting in intrinsic changes

to the material's hardness. These intrinsic effects do not preclude additional extrinsic effects based on changes in grain structure, and so, in addition to diffraction and computation studies, we examined the grain morphology of a range of carbon-doped WB_4 alloy compounds. Figures 5 and S2 show the SEM images of the surface of the alloys of WB_4 with carbon and silicon. In the case of a 1:4.5 metal-to-boron ratio, both carbon and silicon result in reduced grain sizes at low concentrations, primarily manifesting at 6–8 atom % addition for carbon and 8–10 atom % for silicon, attributed to the rapid cooling caused by their addition. At high amounts of carbon addition, areas corresponding to boron carbide formation can be seen (Figure S2).

Figures 6 and S5 are graphs showing Vickers hardness of the alloys. To reduce the effect of the β -rhombohedral boron present in all samples and ensure an accurate hardness value for the overall sample, 10 indents were made in a line of even spacing across each sample and averaged. In addition, given the presence of the indentation size effect and considering that different loads are relevant for different applications, the

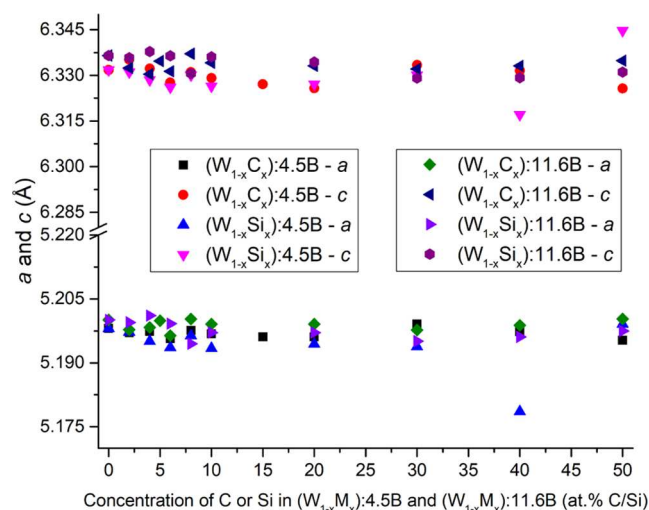


Figure 3. Unit cell parameters a and c for alloys of WB_4 with C and Si, prepared at a nominal metal-to-boron composition of 1:4.5 and 1:11.6, calculated using *Maud*.^{26–30} The literature value for the unit cell parameters of WB_4 are $a = 5.1998(15)$ and $c = 6.3299(19)$.⁵¹

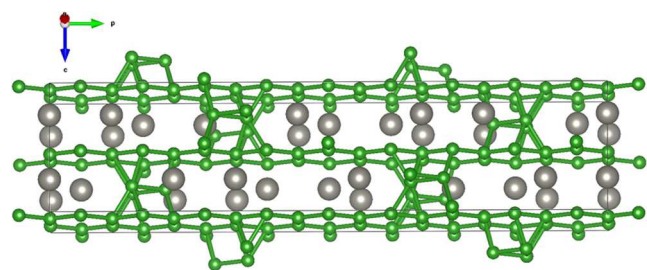


Figure 4. Model $Cmcm$ structure. A characteristic feature of this structure is alternating “rows” of B_3 -trimers, “piercing” the material along the a -axis.

Table 1. Calculated Thermodynamic and Mechanical Properties of Model Structures

impurity	atoms substituted	B_0^a , GPa	H_0^b , eV
pure material	N/A	292.7	−12.6
C	two B atoms in B_{hex} -layer above B_3 -trimers	292.1	−8.7
	four B atoms in B_{hex} -layer above B_3 -trimers	289.8	−5.1
	one B atom in B_3 -trimer	288.6	−7.3
Si	two B atoms in B_{hex} -layer above B_3 -trimer	274.9	−6.9
	one B atom in B_3 -trimer	280.5	−9.2
	B_3 -trimer	281.7	−10.4
Zr	W-occupancy	295.3	−12.9
	W-vacancy	292.0	−12.8

^a B_0 = bulk modulus. ^b H_0 = formation enthalpy.

hardness results for 0.49–4.9 N are presented here. However, since these materials are primarily designed for industrial machining applications, where low loads are a more accurate representation of hardness, all further discussion of the results in this paper will be for 0.49 N. For $(W_{1-x}C_x):11.6B$ (Figure 6, top), the hardness increase at 5 atom % C to 52.2 ± 3.0 GPa, compared to 41.2 ± 1 GPa for the pure phase, correlates with the formation of a fine-grained morphology, but may also have an intrinsic component (Figure 5, top), while the second

increase at 50 atom % C to 51.8 ± 6.1 GPa appears to be the result of extrinsic effects due to the formation of boron carbide.²⁹ For $(W_{1-x}Si_x):11.6B$ (Figure 6, bottom), the hardness maximum at 2 atom % Si of 50.5 ± 2.5 GPa again correlates with changes in grain morphology (Figure 5, bottom), while at higher amounts of silicon addition, the hardness plateaus at ~ 42 GPa. In the case of $(W_{1-x}C_x):4.5B$ (Figure S5, top), similar trends are observed, but with lower absolute hardness values, where the hardness first increases to 38.0 ± 3.8 GPa at 6 atom % C, compared to 30.8 ± 2.8 GPa¹⁸ for the pure phase, which correlates with changes in morphology and grain size (Figure S2, top), while the second hardness increases to 53.4 ± 6.6 GPa at 50 atom % C clearly results from the formation of the superhard boron carbide phase.²⁹ Similarly for $(W_{1-x}Si_x):4.5B$ (Figure S5, bottom), the hardness maxima at 8–10 atom % Si of 38.7 ± 3.0 and 40.0 ± 2.2 GPa, respectively, correspond to changes in grain morphology (Figure S2, bottom), while at higher amounts of silicon addition, the hardness plateaus at ~ 36 GPa.

To complement the pure addition of C, Si, and Zr to $WB_{4,2}$, a few more complex combinations were produced. Specifically, C was added to two WB_4 alloy compositions of interest: the single-phase alloy with a WB_4 structure prepared with a stoichiometric amount of boron— $(W_{0.67}Ta_{0.33}):4.5B$;¹⁸ and an alloy with 8 atom % zirconium addition— $(W_{0.92}Zr_{0.08}):11.6B$ ¹⁴—which resulted in the most nanostructured grain morphology with the highest hardness value for WB_4 -based alloys. The case of $(W_{0.92}Si_{0.08}):11.6B$ was not chosen for C addition as it represents results similar to the Zr version but with a lower hardness value. In the case of $(W_{0.67}Ta_{0.33}):4.5B$, when carbon was added, a secondary lower boride (WB_2) started to form at about 20 atom % C, which can be explained by the fact that as boron carbide forms, it lowers the amount of available boron (Figure S3). The grain morphology does not change drastically, until ~ 40 atom % carbon addition (Figure S4), at which point, the boron carbide phase starts to generate a lamellar decomposition pattern.³⁰ In agreement with these observations, indentation data show only a gradual increase in hardness to a maximum of 44.6 ± 7.5 GPa at 100 atom % C addition, mainly due to the formation of boron carbide. No peaks in the hardness as a function of C addition are observed, as in the case of C or Si substituted into $WB_{4,2}$, suggesting only grain size and compositional effects are at play. By contrast, in the case of $(W_{0.92}Zr_{0.08}):11.6B$, the nanomorphology is lost immediately upon the addition of carbon, resulting in a hardness decrease from 55.9 ± 2.8 GPa¹⁴ for the pure phase, to ~ 45 GPa with low carbon addition, and back up to 52.4 ± 6.9 GPa at 100 atom % C, again due to the formation of boron carbide (Figure S6). For $(W_{0.92}Zr_{0.08}):11.6B$, lower borides (WB_2) do not form until ~ 80 atom % C addition because of the large amount of excess boron (Figure S3). These results make two things clear: (1) small compositional changes can produce dramatic morphological changes, which can, in turn, dramatically change the bulk hardness of the composite through extrinsic effects, and (2) adding substituents like carbon can dramatically change the phase composition of a sample, resulting in a complex mixture of effects.

Because of the large number of possible combinations and the interplay of intrinsic and extrinsic effects, we chose three of the hardest phases for further study. The Vickers hardness values and grain morphologies of these three compositions— WB_4 with 8 atom % Zr, 4 atom % C, and 2 atom % Si—can be seen in Figure 7. The metal and the two nonmetals have a

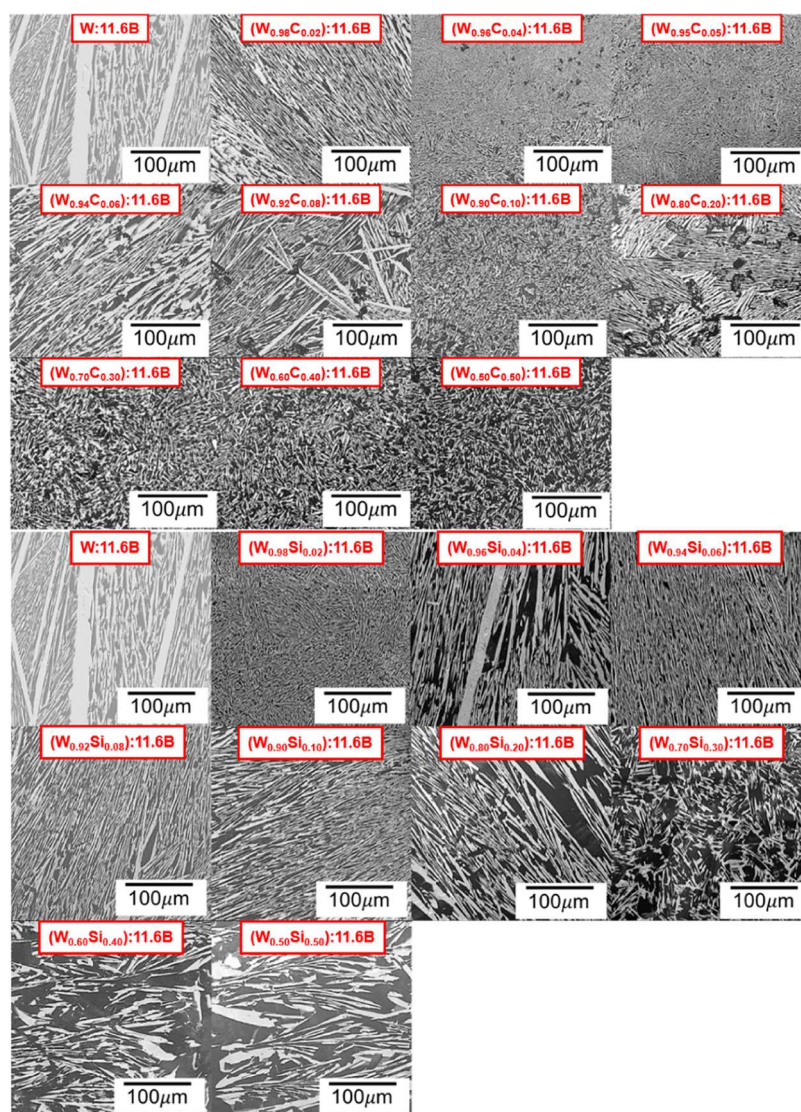


Figure 5. SEM images for alloys of WB_4 with a nominal composition of (top) $(\text{W}_{1-x}\text{C}_x):11.6\text{B}$ and (bottom) $(\text{W}_{1-x}\text{Si}_x):11.6\text{B}$ showing a change in surface morphology associated with the effects of carbon and silicon and secondary phase formation. All SEM images were taken at 1000 $\times$ magnification; the scale bars are 100 μm .

similar effect on the grain morphology, resulting in small grains for all substituted compositions. The key question is to what extent is the increased hardness discussed above a result only of this decreased grain size, given that all elements have the potential to substitute into the host lattice?

Although Vickers microindentation provides a direct measurement of a material's hardness, it often does not afford sufficient mechanical insight into intrinsic properties or explain the effects of dopant positions on the material's bonding motif. Our goal here is to use high-pressure studies to understand the mechanisms for tunable hardness from doping WB_4 with boron-like light elements (C and Si) as well as transition metals (Zr). Previously, we demonstrated that the WB_4 structure is stabilized by boron with a ratio of 1:11.6 and a small amount of secondary transition metal. Samples with nominal compositions of $(\text{W}_{0.96}\text{C}_{0.04}):11.6\text{B}$ and $(\text{W}_{0.92}\text{Zr}_{0.08}):11.6\text{B}$, especially, exhibit the best homogeneity in morphologies, essentially single-phase WB_4 with remarkable hardness. For simplicity, we now abbreviate them as $\text{W}_{0.96}\text{C}_{0.04}\text{B}_4$ and $\text{W}_{0.92}\text{Zr}_{0.08}\text{B}_4$ to clarify the structure of the

sample and the percentage of the dopants, ignoring excess boron.

By compressing a sample under nonhydrostatic stress in a diamond anvil cell, radial X-ray diffraction can be readily collected at incremental pressure steps (up to 45 GPa) *in situ* to provide information about the evolution of the unit cell volume and also lattice-specific measurements of differential strain and predominant slip planes in the material. In the radial geometry, diffraction data are collected at a range of angles with respect to the low and high-stress directions, and the stress state of the sample under nonhydrostatic compression can be determined according to lattice strain theory, as explained in Figures S7–S9. The integrated “cake” patterns, azimuthal angle (η) vs diffraction angles (2θ) were reported at both low and high pressure. At low pressure, the nearly straight diffraction lines of the “cake” patterns are due to the hydrostatic stress state. However, at high pressure, sinusoidal variations of the diffraction lines occur due to nonhydrostatic stress so that the diffraction lines deviate to a higher angle (2θ) in the high-stress direction ($\varphi = 0^\circ$) and to a lower angle (2θ) in the low-stress direction ($\varphi = 90^\circ$). The waviness of the

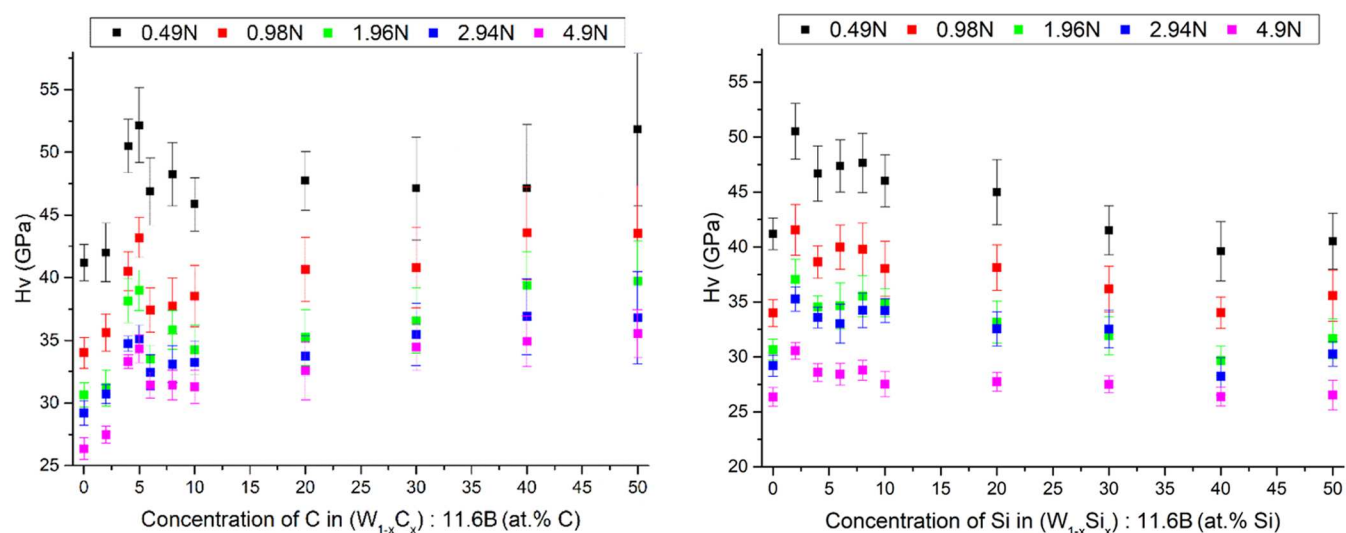


Figure 6. Vickers microindentation hardness of alloys with a nominal composition of (left) $(W_{1-x}C_x):11.6B$ and (right) $(W_{1-x}Si_x):11.6B$ alloys at low (0.49 N) to high (4.9 N) loading.

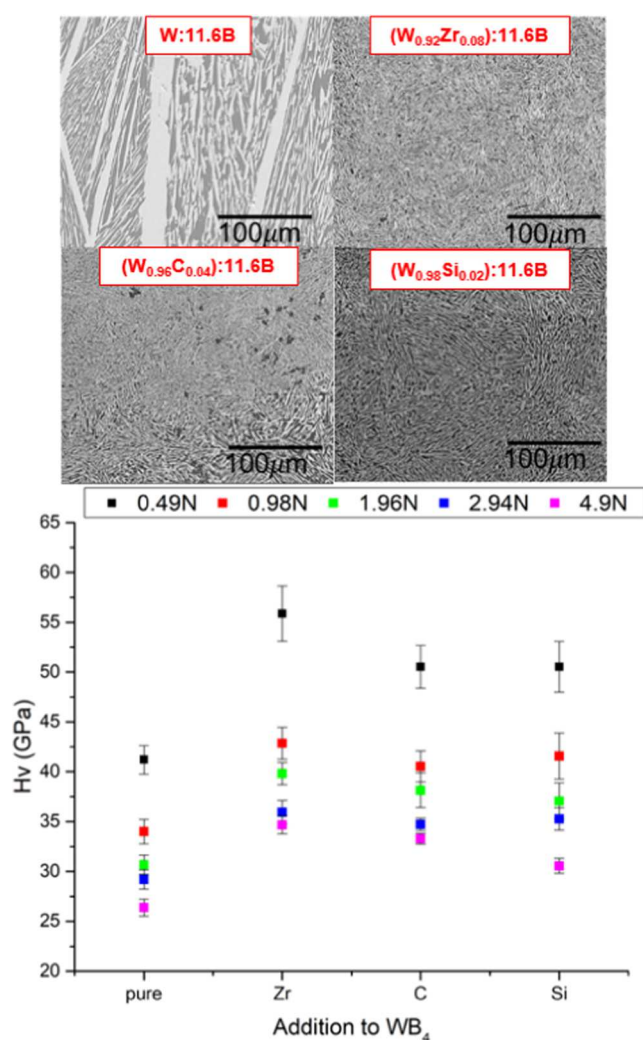


Figure 7. Vickers microindentation hardness and SEM images of WB_4 alloys with a nominal composition of $(W_{1-x}M_x):11.6B$, where M = zirconium ($x = 0.08$), carbon ($x = 0.04$), and silicon ($x = 0.02$) at low (0.49 N) to high (4.9 N) loading. All SEM images were taken at 1000 $\times$ magnification; the scale bars are 100 μm .

diffraction lines indicates the lattice-supported strains, which will be further discussed in Figure 8. In the one-dimensional (1-D) diffraction patterns, a clear shift of the peaks obtained at $\varphi = 54.7^\circ$ (the magic angle) to higher angles at higher pressure indicates a decrease in the lattice spacing with greater compression, and the peak broadening implies strain inhomogeneity. The pressure-dependent d -spacings of the (002), (101), and (110) planes at the quasi-hydrostatic condition ($\varphi = 54.7^\circ$, magic angle), are plotted in Figure 8. Examples of the full description of the d -spacings at all angles are shown in Figure 9, which demonstrates the linear correlation between d -spacings and $(1 - 3 \cos^2 \varphi)$ for the selected planes of WB_4 solid solutions at the highest pressure. According to eq 3, the slope of each line yields the corresponding $Q(hkl)$, and the intercept gives the d -spacing under quasi-hydrostatic compression. The differential strain (t/G), which is the ratio of differential stress (t) to shear modulus (G), can be directly determined from the $Q(hkl)$ value, as shown in eq 4.

In Figure 10, the $t(hkl)/G$ ratio increases linearly with pressure at the beginning, then levels off, increases slowly, and eventually plateaus at 30 GPa. The plateau indicates the onset of plastic deformation, where the bonding starts to break and the lattice dislocations become irreversible. The planes with a higher $t(hkl)/G$ plateau value (differential strain) can be deformed to a greater extent before undergoing plastic deformation, and the plane with the lowest $t(hkl)/G$ plateau slips with the lowest deformation.

As seen in Figure 10, $W_{0.96}C_{0.04}B_4$ supports higher differential strain, $t(hkl)/G$, than pure WB_4 in all three lattice planes of choice, indicating lattice planes in $W_{0.96}C_{0.04}B_4$ can undergo more deformation before bond breaking and are less prone to slip than in pure WB_4 . In other words, $W_{0.96}C_{0.04}B_4$ is intrinsically harder than WB_4 . In $W_{0.96}C_{0.04}B_4$, the (002) plane, parallel to the layers of boron and tungsten atoms, supports the highest differential strain, followed by the (110) plane and then the (101) plane. In pure WB_4 , however, the (110) and (101) planes have almost identical differential strain. The fact that the (002) plane is greatly enhanced and the (110) plane is less prone to slip than the (101) plane in $W_{0.96}C_{0.04}B_4$ suggests that the bonding in the c axis is particularly strengthened by

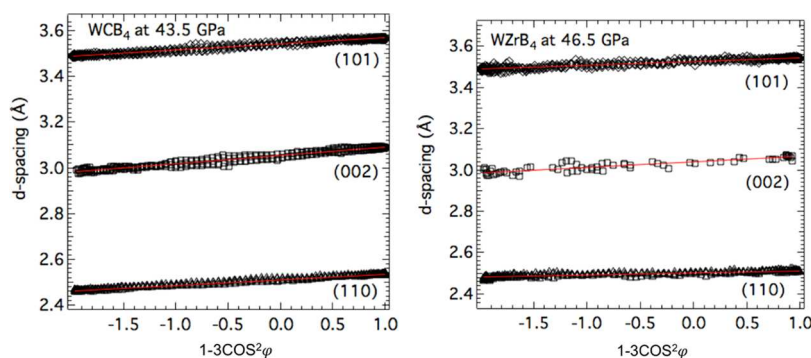


Figure 8. Linearized plots of d -spacings for $W_{0.96}C_{0.04}B_4$ (left) and $W_{0.92}Zr_{0.08}B_4$ (right) as a function of $(1-3\cos^2\varphi)$ at the highest pressure. Solid lines are the best linear fit to the data.

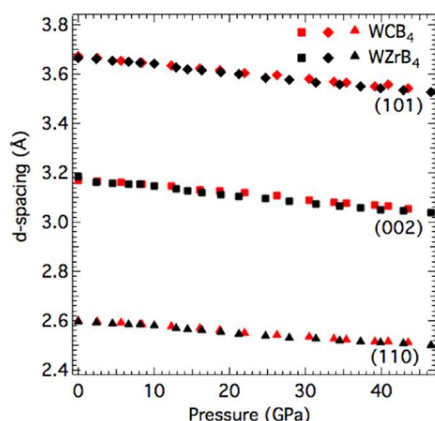


Figure 9. Selected d -spacings vs pressure collected at $\varphi = 54.7^\circ$ for $W_{0.96}C_{0.04}B_4$ and $W_{0.92}Zr_{0.08}B_4$.

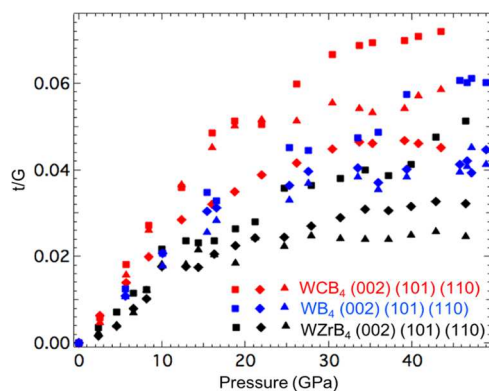


Figure 10. Ratio of differential stress to shear modulus (t/G) for pure WB_4 (blue) compared to WB_4 with 8 atom % Zr (black) and 4 atom % C (red) addition.

doping with carbon and confirms the computational results that carbon substitution into the boron sheets right above the boron trimer, enhancing the $C_{\text{layer}}-B_{\text{cluster}}$ bonds (*vide infra*). This suggests that the addition of carbon maintains the cage structure and strengthens the cross-links between the interlayers, contributing to the enhanced intrinsic hardness of $W_{0.96}C_{0.04}B_4$.

When 8 atom % zirconium is doped into WB_4 , the resultant solid solution is the hardest of any of the materials discussed here, but radial diffraction studies show decreased differential strain in the (002), (100) and (101) planes compared to pure WB_4 (Figure 10). The decrease in the differential strain in all

three lattice planes in $W_{0.92}Zr_{0.08}B_4$ suggests that the overall ability of the material to resist slip has been disrupted by the addition of Zr. Given the importance of the pseudo-cage structure's contribution to the hardness of WB_4 , it is hypothesized that the addition of Zr disrupts this structure and therefore reduces the material's overall hardness. This is further supported by the weakening of the c axis that is also observed from strain anisotropy. This indicates that the (101) plane supports higher differential strain than the (110) plane in $W_{0.92}Zr_{0.08}B_4$, and is consistent with computational results that Zr weakens bonding between interlayers by doping into the tungsten vacancies.³¹ The fact that $W_{0.92}Zr_{0.08}B_4$ has the highest Vickers hardness among pure WB_4 and its solid solutions but has lower plateau differential strain values for all lattice planes suggests that the enhanced Vickers hardness by doping Zr largely results from improved extrinsic hardness due to the very small grain sizes found in this material. Vicker's hardness is sensitive to both intrinsic and extrinsic effects, while the high-pressure experiments explore only a material's microscopic deformation, which contributes to the intrinsic hardness.

The Si-doped sample posed an experimental challenge because the highly elongated grains produced a strong texture in the radial diffraction experiment, which resulted in insufficient data for some lattice planes to analyze the differential strain. As shown in Figure S9, the Si-doped sample exhibits strong texture even at pressure as low as 1.7 GPa. The few lattice planes that could be analyzed are plotted in Figure S1A, along with the data for the undoped, C-doped, and Zr-doped materials. While the quality of the data is fairly poor, it is clear that the differential strain is similar to or lower than that of pure WB_4 , indicating that, similar to the Zr-doped case, the increase in hardness likely arises primarily from extrinsic effects.

The rigid cage structure along the c -direction in the WB_4 system not only supports a high differential strain but also resists great hydrostatic compression (high bulk modulus). From fitting the third-order Birch–Murnaghan equation of state in terms of normalized pressure and Eulerian strain, the bulk moduli for $W_{0.92}Zr_{0.08}B_4$ and $W_{0.96}C_{0.04}B_4$ were determined to be 329 ± 4 GPa ($K'_0 = 2$) and 390 ± 9 GPa ($K'_0 = 0.6$), respectively (Figure 11). The bulk modulus of $W_{0.92}Zr_{0.08}B_4$ is within the range of the bulk modulus of WB_4 (326–339 GPa), and other borides,^{32,33} while $W_{0.96}C_{0.04}B_4$ has a higher bulk modulus than WB_4 . While having high incompressibility is beneficial to a hard material, the two properties are not necessarily linked. As such, the difference

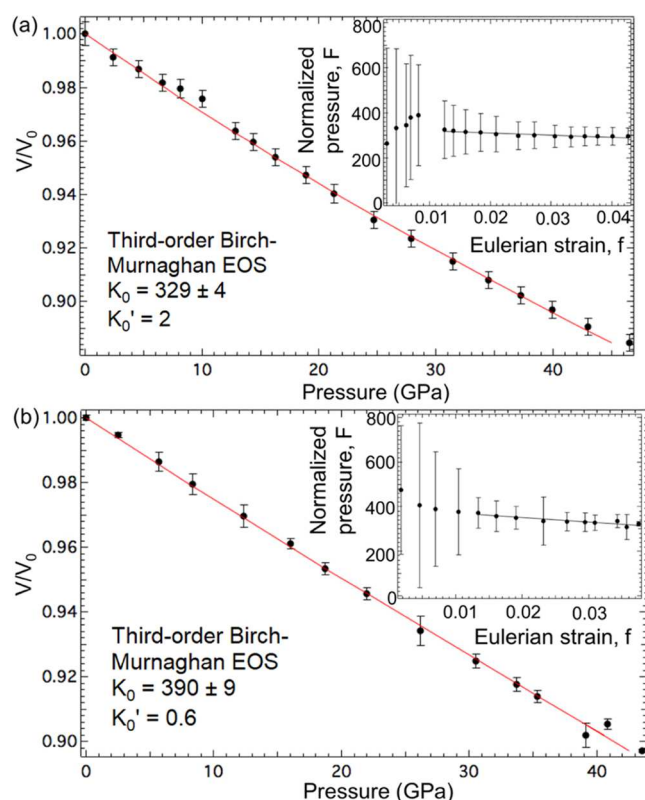


Figure 11. Evolution of the unit cell volume for $W_{0.92}Zr_{0.08}B_4$ (a) and $W_{0.96}C_{0.04}B_4$ (b) as a function of the pressure under nonhydrostatic compression. The volume was measured at $\varphi = 54.7^\circ$. The red solid line is the best fit to the third-order Birch–Murnaghan equation of state (EOS). The inset is the third-order Birch–Murnaghan EOS plotted in terms of normalized pressure and Eulerian strain. The straight line in the inset plot yields the ambient-pressure bulk modulus.

between the bulk moduli of $W_{0.96}C_{0.04}B_4$ and $W_{0.92}Zr_{0.08}B_4$ is not a result of the changes in the pseudo-cage structure as seen with the differential strain changes. Rather, it is likely that the additional electron density provided by the C addition increases the bulk modulus. An accurate bulk modulus for the Si-doped sample could, unfortunately, not be calculated.

To validate these conclusions and clarify the effects of C, Zr, and Si dopants on the local rigid cage structure and its influence on the mechanical properties of the material, we return to theoretical calculations. First, bulk moduli, B_0 , were calculated for structures with impurities in several different positions (Table 1). DFT-based B_0 values are significantly underestimated compared to the experimental values. The discrepancy can be attributed to the use of a GGA functional (PBE), which suffers from delocalization error resulting in underestimated B_0 by $\sim 9\%$;³⁴ poor treatment of van der Waals interactions; and disregard for relativistic effects in W. We have attempted to recalculate the bulk modulus for pure and C-doped structures with HSE06^{35,36} hybrid functionals and observed an increase in B_0 , but still not to the level of the experimental results. We therefore used the PBE functional for its greater computational efficiency and used DFT calculations for trends only. The inclusion of Si decreases the computed B_0 of $WB_{4.2}$, while the inclusion of C leaves the computed B_0 practically unchanged. The introduction of Zr in either position marginally increases the computed B_0 .

A better measure of the mechanical hardness is the shear modulus. Accessing it computationally for such a large supercell is prohibitively expensive, and thus, we infer information about stability against shear through the analysis of electron density using the quantum theory of atoms in molecules (QTAIM).³⁷ QTAIM analyzes the topology of the quantum mechanical charge density, ρ . Specifically, ρ is rigorously partitioned into atomic basins, defined by zero-flux surfaces where the normal vector at any point on the surface is orthogonal to the gradient of electron density ($\nabla\rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0$). There are 4 types of critical points (CPs) in ρ : nuclear, bond, ring, and cage CPs, defined by the curvature of $\rho(\mathbf{r})$ at that point. A bond CP (BCP), of most interest to this study, is a maximum in 2 spatial directions and a minimum in 1 spatial direction; a ring CP (RCP) is a maximum in 1 spatial direction and a minimum in 2 spatial directions; and a cage CP (CCP) is a minimum in all 3 spatial directions. Topological quantities include curvature and $\nabla^2\rho(\mathbf{r})$. Characteristics of ρ at CPs are telling of material properties, such as mechanical stability.

Since chemical bonding is a local effect, and also the bonding is largely covalent in $WB_{4.2}$, we used a smaller $2 \times 2 \times 1$ supercell with a single B_3 -trimer, isolated from other trimers. The relevant QTAIM graphs are shown in Figure 12 and the BCPs discussed are shown in Figure 13. Due to the pseudo-layered nature of the material, the weakest slip system in $WB_{4.2}$ is the shear in the [001] plane. Therefore, the bonds connecting hexagonal layers either through B_3 -trimers or through metal atoms are essential for strengthening $WB_{4.2}$ against shear. The strongest bond formed in the C-doped $WB_{4.2}$ is the 2-center bond between B in the B_3 -trimer and C in the B_{hex} -layer (Figure 12). It has the highest electron density and lowest Laplacian density in the entire structure. The formation of the strong $C_{\text{layer}}-B_{\text{cluster}}$ bond is likely related to the resistance of the material to shear. The bonds formed with other impurities generally have a lower electron density and higher positive Laplacians, associated with bond weakening. For instance, the substitution of W with Zr in Wyckoff 2c leaves the interlayer bonding unchanged or weakens it, while substitution of Zr in the W-vacancy always depletes the electron density of interlayer bonds (Table 2). This result is consistent with the experimental observation that the plateau differential strain observed through high-pressure radial diffraction is actually lower in $W_{0.92}Zr_{0.08}B_4$ than in WB_4 .

An extreme example of bond weakening is Si, upon substituting itself for the entire B_3 -cluster. The bonds it forms with the B-sheets are characterized by small $\rho(\vec{r})$ and near-zero $\nabla\rho(\vec{r})$. While the metal dopants generally slightly weaken $B_{\text{cluster}}-B_{\text{sheet}}$ (lower in $\rho(\vec{r})$ and higher in $\nabla\rho(\vec{r})$), the Si impurity replaces those bonds with significantly weaker bonds. This may explain why the hardness is only slightly increased in Si-doped $WB_{4.2}$, despite a dramatic reduction in grain size, and suggests that hardness enhancement in Si-doped $WB_{4.2}$, like that in Zr-doped $WB_{4.2}$, is dominantly extrinsic/grain size induced in nature.

CONCLUSIONS

Tungsten tetraborides have been extensively explored due to their unique rigid pseudo-cage structures that result in high hardness. The partially occupied tungsten sites and voids in the crystal structure also make WB_4 of particular interest for enhancing the hardness by doping heteroatoms into the WB_4 lattice. Because of this, extensive work has been carried out to enhance the hardness of WB_4 by doping heteroatoms into the

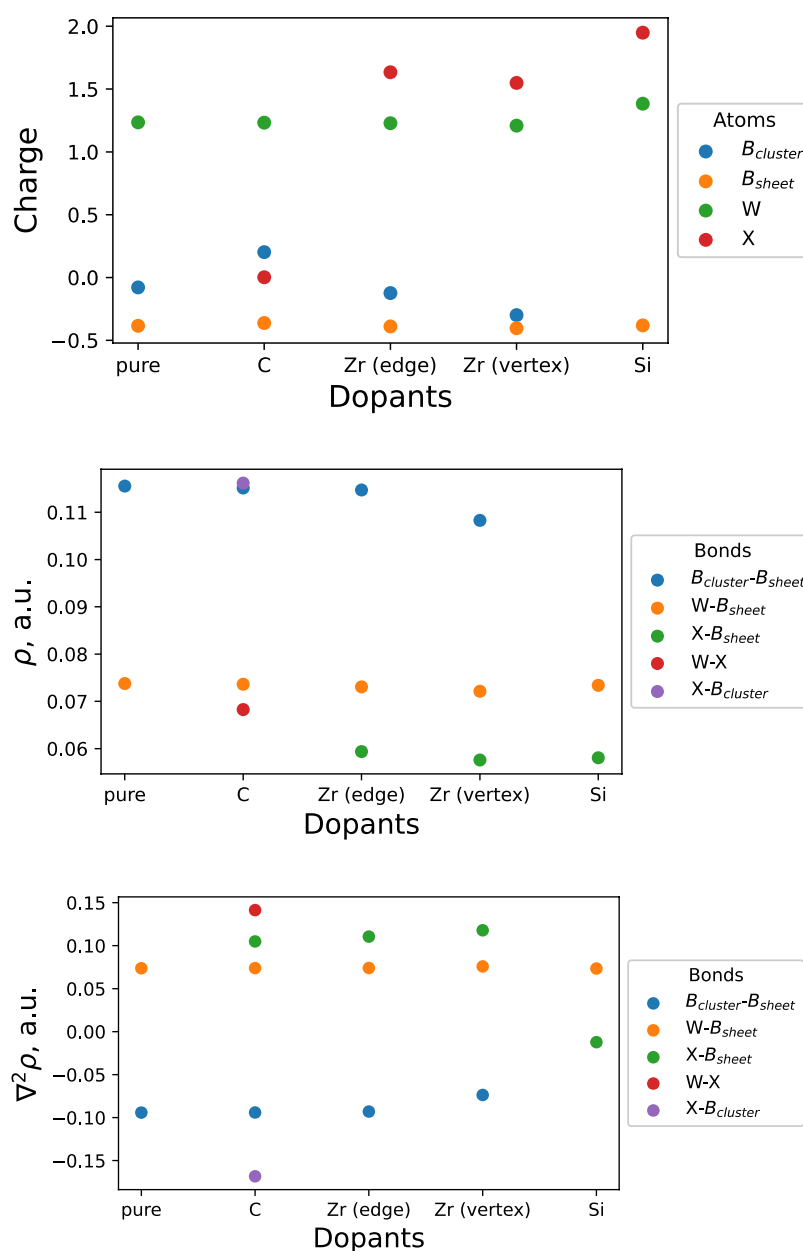


Figure 12. QTAIM analysis of BCPs for model structures. (a) Average Bader atomic charges in model structures. (b) Average electron density at BCPs, connecting “layers” of the material. Average Laplacian at BCPs, connecting “layers” of the material.

crystal lattice, modifying the overall composition of composite materials, and introducing and/or modifying grain boundaries. The challenge, exemplified in this work, is that very often, all of these processes occur simultaneously. As a result, it is difficult to develop a predictive understanding of the most effective ways to enhance hardness. In the current study, significant decreases in grain size were observed in all solid solutions, and, in parallel, the hardness was greatly enhanced. While the significant decrease of grain size in these solid solutions suggests extrinsic or grain-boundary-based hardening effects, lattice-specific strain analysis indicates that such a conclusion is not uniformly true in these materials. High-pressure studies, together with computational work, demonstrate significant change of bonding upon doping, in both the positive and negative directions. Specifically, doping carbon into WB_4 strengthens the bonding in the cage structure, resulting in better resistance to plastic deformation. In contrast, doping Zr

and Si into WB_4 disrupts the cage structure, consequently leading to a weaker intrinsic strength. For both Zr and Si, however, the reduced grain size and potential improved grain boundary strength compensate for the reduced bond strength, resulting in enhanced hardness, but a reduction in the plateau value of the differential strain. This work thus shows that through a combination of morphological studies, high-pressure diffraction experiments, and first-principles calculations the hardening effects in a highly complex, multiphase material like doped WB_4 can be thoroughly understood from both intrinsic and extrinsic perspectives.

EXPERIMENTAL PROCEDURE

Synthesis of WB_4 and Solid Solutions. Metal boride samples were synthesized by arc-melting weighed out amounts of metal and boron. The prepared phases were partly crushed into powder and analyzed by laboratory powder X-ray diffraction (PXRD) and partly

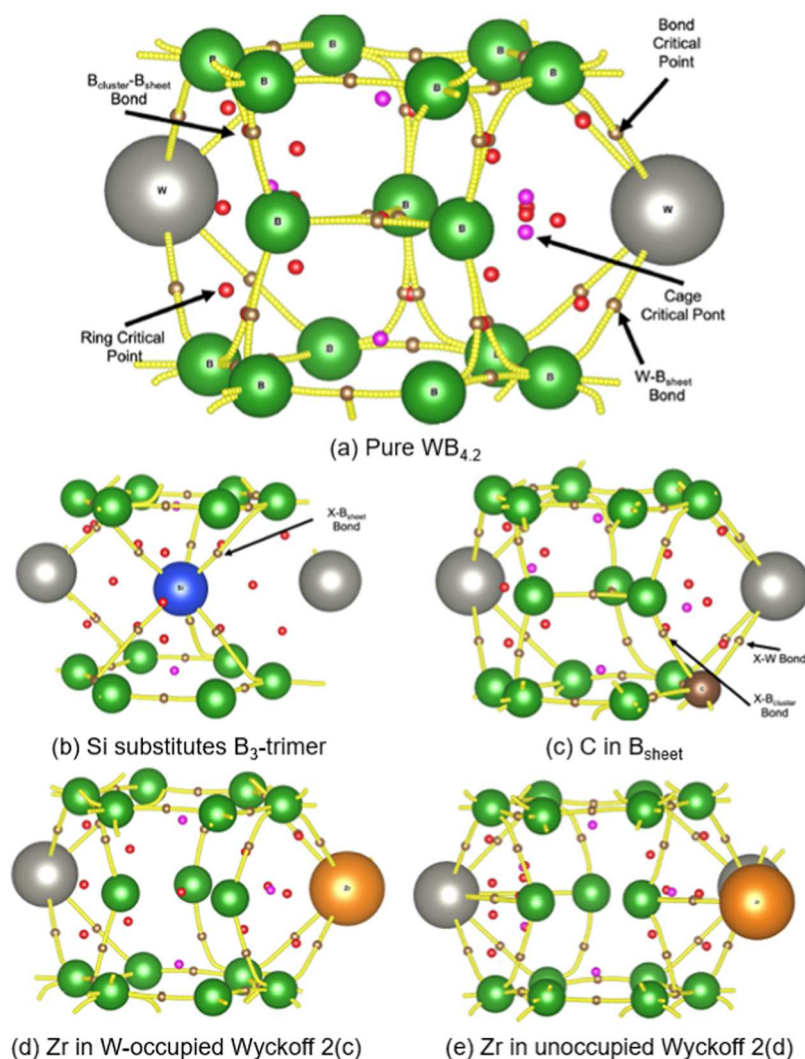


Figure 13. Bonding QTAIM analysis of model structures with selected impurities. Point descriptions: Bond CPs, brown; Ring CPs, red; Cage CP, magenta. Lines of gold critical points depict bond paths.

Table 2. Electron Density and Laplacians of BCPs at $B_{\text{cluster}}-B_{\text{layer}}$ bonds (or $B_{\text{cluster}}-C_{\text{layer}}$ in Case of C Dopant)

	electron density, au	Laplacian, au
pure	0.115	−0.996
C	0.117	−0.156
Zr (edge)	0.114	−0.998
Zr (vertex)	0.107	−0.06

encased in epoxy resin and polished. The polished samples were used for Vickers hardness microindentation and scanning electron microscopy (SEM). Samples were further analyzed using non-hydrostatic *in situ* high-pressure radial X-ray diffraction performed in a diamond anvil cell at synchrotron beamline 12.2.2 of the Advanced Light Source (ALS, Lawrence Berkeley National Laboratory).

Alloys of WB_4 with carbon and silicon were prepared using tungsten (99.95%, Strem Chemicals), amorphous boron (99+%, Strem Chemicals), tantalum (99.9%, Strem Chemicals), silicon (99.9%, American Elements), and tungsten carbide (99.5%, Strem Chemicals). For these alloys, the M/B ratio was kept at 1:4.5 and 1:11.6. For samples with a nominal composition of $(W_{1-x}C_x):4.5B$, $(W_{0.67}Ta_{0.33}):C_x:4.5B$, $x = 0.00, 0.02, 0.04, 0.06, 0.08, 0.10, 0.15, 0.20, 0.30, 0.40, 0.50$; samples with a nominal composition of $(W_{1-z}C_z):11.6B$, $(W_{0.92}Zr_{0.08}):C_z:11.6B$, $z = 0.00, 0.02, 0.04, 0.05,$

$0.06, 0.08, 0.10, 0.20, 0.25, 0.30, 0.40, 0.50$; and for samples with a nominal composition of $(W_{1-t}Si_t):4.5B$, $(W_{1-t}Si_t):11.6B$, $t = 0.00, 0.02, 0.04, 0.06, 0.08, 0.10, 0.20, 0.25, 0.30, 0.40, 0.50$.

Boron and metal powders in appropriate ratios were mixed in an agate mortar to ensure homogeneity. A hydraulic press (Carver) was used to press the mixtures of powders into pellets with a diameter of 1.27 cm (0.5 in.) under a 10-ton load. The pressed pellets were then placed in an arc-melting chamber on top of a water-cooled copper hearth. The chamber was then sealed and evacuated under vacuum for 20 min, followed by filling with argon; this was repeated at least 4 times. Before arc-melting the samples, getters made of titanium and zirconium were melted in order to “absorb” any trace oxygen, and finally, the samples were then arc-melted using $I > 70$ A (typically 145 A) for 1–2 min. The samples were heated until molten, flipped, and re-arc-melted at least 2 times to ensure homogeneity.

The prepared samples were separated into two halves using a diamond saw (Ameritool, Inc.), with one half crushed into sub-40 μm powder for powder X-ray diffraction analysis (PXRD) using a Plattner-style crusher, while the other half was encapsulated into epoxy for scanning electron microscopy (SEM) and Vickers hardness testing using an epoxy/hardener set (Allied High Tech Products, Inc.).

Characterization. In order to polish the samples to an optically flat surface, SiC papers (120–1200 grit sizes, Allied High Tech Products, Inc.) and diamond films with particle sizes ranging from 30

to 1 μm (South Bay Technology, Inc.) were used on a semiautomated polishing station (South Bay Technology, Inc.).

To establish the purity and phase composition of the samples, PXRD and SEM techniques were used. PXRD was performed on a Bruker D8 Discover Powder X-ray Diffractometer (Bruker Corporation, Germany) using a Cu $K\alpha$ X-ray beam ($\lambda = 1.5418 \text{ \AA}$) in the $5\text{--}100^\circ 2\theta$ range with a step size of 0.0353° , scan speed of $0.1055^\circ/\text{sec}$ and time per step of 0.3 s . The Joint Committee on Powder Diffraction Standards (JCPDS) database was used to identify the phases present in the samples. *Maud* software was used to perform the unit cell refinements.^{38–42}

Vickers Hardness Test. Hardness measurements were performed on polished samples using a load-cell-type multi-Vickers hardness tester (Leco) with a pyramidal diamond indenter tip. Under each applied load: 0.49, 0.98, 1.96, 2.94, and 4.9 N, 10 indents were made in randomly chosen spots on the sample surface. The lengths of the diagonals of the indents were measured using a high-resolution optical microscope, Zeiss Axiotech 100HD (Carl Zeiss Vision GmbH, Germany) with $500\times$ magnification. Vickers hardness values (H_v in GPa) were calculated using the following formula (eq 1) and the values of all 10 indents per load were averaged

$$H_v = \frac{1854.4F}{d^2} \quad (1)$$

where d is the arithmetic average length of the diagonals of each indent in microns and F is the applied load in Newtons (N).

High-Pressure Experiment. Nonhydrostatic *in situ* high-pressure radial X-ray diffraction was performed in a diamond anvil cell at synchrotron beamline 12.2.2 of the Advanced Light Source (ALS, Lawrence Berkeley National Laboratory). Crushed powder of the samples ($\text{W}_{0.96}\text{C}_{0.04}$: 11.6 B and $\text{W}_{0.92}\text{Zr}_{0.08}$: 11.6 B) was loaded into a laser-drilled hole ($\sim 60 \mu\text{m}$ in diameter, $\sim 60 \mu\text{m}$ in depth) in a $\sim 400 \mu\text{m}$ diameter boron gasket made of amorphous boron and epoxy. Both samples adopt the WB_4 structure; therefore, we abbreviate them as $\text{W}_{0.96}\text{C}_{0.04}\text{B}_4$ and $\text{W}_{0.92}\text{Zr}_{0.08}\text{B}_4$ when we mention these two samples in the text. A small piece of Pt foil ($\sim 20 \mu\text{m}$ diameter) was placed on top of the sample to serve as an internal pressure standard. A monochromatic X-ray beam ($\lambda = 0.4959 \text{ \AA}$, spot size = $30 \mu\text{m} \times 30 \mu\text{m}$) was passed through the sample, which was compressed between two diamond tips up to 60 GPa of pressure, and two-dimensional (2-D) diffraction data were collected by using a MAR-345 image plate and FIT2D software. A cerium dioxide (CeO_2) standard was used to calibrate the detector distance and orientation. The stress state of the sample under nonhydrostatic compression was analyzed by Igor Pro (WaveMetrics, Inc.) based on lattice strain theory.

In the radial geometry, the X-rays are directed onto the sample through the boron gasket and between the diamond culets. The collected 2-dimensional diffraction patterns contain information on the d -spacings in the low- and high-stress directions and at all intermediate angles. The stress in the sample under uniaxial compression is described by eq 2

$$\sigma = \begin{bmatrix} \sigma_1 & 0 & 0 \\ 0 & \sigma_1 & 0 \\ 0 & 0 & \sigma_3 \end{bmatrix} = \begin{bmatrix} \sigma_p & 0 & 0 \\ 0 & \sigma_p & 0 \\ 0 & 0 & \sigma_p \end{bmatrix} + \begin{bmatrix} -t/3 & 0 & 0 \\ 0 & -t/3 & 0 \\ 0 & 0 & -2t/3 \end{bmatrix} \quad (2)$$

where σ_1 is the minimum stress along the radial direction, σ_3 is the maximum stress in the axial direction, σ_p is the hydrostatic stress component, and t is the differential stress, which gives a lower-bound estimate of yield strength. Each line in the two-dimensional cake pattern corresponds to a d -spacing and starts as a straight line at low pressure, indicating a hydrostatic stress state. At high pressure, the lines deviate to lower angles in the low-stress direction (σ_1) and to higher angles in the high-stress direction (σ_3) (Figures S7–S9). The integrated one-dimensional diffraction pattern at the magic angle shifts to higher angles with increasing pressure as the lattice spacing decreases upon compression (Figures S7–S9). The d -spacing is calculated by

$$d_m(hkl) = d_p(hkl)[1 + (1 - 3\cos^2 \varphi)Q(hkl)] \quad (3)$$

where d_m is the measured d -spacing, d_p is the d -spacing under the hydrostatic component of the stress, φ is the angle between the diffraction normal and axial directions, and $Q(hkl)$ is the lattice strain under the uniaxial stress condition. The differential stress, t , is directly related to the differential strain, $t(hkl)/G(hkl)$, by

$$t(hkl) = 6G(hkl)Q(hkl) \quad (4)$$

where $G(hkl)$ is the shear modulus of the specific lattice plane. The lattice parameters at each pressure calculated from the d -spacings at $\varphi = 54.7^\circ$ are summarized in Tables S1A and S2. Incompressibility was then determined using the third-order Birch–Murnaghan equation of state (EOS), which can be written as

$$P = \frac{3}{2}K_0 \left[\left(\frac{V_0}{V} \right)^{7/3} - \left(\frac{V_0}{V} \right)^{5/3} \right] \left[1 + \frac{3}{4}(K'_0 - 4) \left[\left(\frac{V_0}{V} \right)^{2/3} - 1 \right] \right] \quad (5)$$

where P is the pressure, K_0 is the bulk modulus, V is the volume, V_0 is the undeformed unit cell volume, and K'_0 is the derivative of K_0 with respect to P .

Computation Details. The sampling of the B_3 -cluster distributions within a $3 \times 2 \times 1$ supercell was performed with Site Disorder Occupancy.⁴³ All quantum mechanical calculations in this work were performed within the GGA PBE^{44,45} functional, as implemented in VASP.^{46–48} The kinetic energy cutoff of 750 eV together with the second order Methfessel–Paxton approximation with $\sigma = 0.2$ were used. The first Brillouin zone was sampled using γ -centered Monkhorst–Pack Grids with k -point mesh density of $2\pi \times 0.025 \text{ \AA}^{-1}$. All structures were relaxed until the forces on each atom were $\leq 0.01 \text{ eV}$.

Quantum Theory of Atoms and Molecules (QTAIM) calculations were performed using Critic2 software.^{49,50} A recursive subdivision of the Wigner–Seitz cell algorithm was used to locate critical points such that the Morse number of the resulting graph equals zero. The integration of atomic basins for Bader charge calculations in the Yu and Trinkle (YT)⁵¹ method was utilized. QTAIM is a method to analyze the topology of the electron density, $\rho(\vec{r})$. In QTAIM, each atom is associated with a nuclear critical point (NCP)—a local maximum in $\rho(\vec{r})$, and an atomic basin—a portion of space surrounded by a zero-flux surface ($\nabla\rho(\vec{r})$). A Bader charge of an atom is the difference between the number of valence electrons and the integral of $\rho(\vec{r})$ within the atomic basin. $\rho(\vec{r})$ contains four types of critical points: nuclear critical points (NCP) have three negative eigenvalues of the Hessian (local maxima); bond critical points (BCP) have two negative and one positive eigenvalues of the Hessian (saddle points); ring critical points (RCP) have one positive and two negative eigenvalues of the Hessian (second order saddle points); and cage critical points (CCP) have three positive eigenvalues of the Hessian (local minima). Paths that trace the direction of the maximum gradient of $\rho(\vec{r})$ between two NCPs are called bond paths, defining a bond. A point of intersection of a bond path and an atomic basin surface is a BCP, and it determines the properties of the bond. In this work, we used the electron density, $\rho(\vec{r})$, at a BCP (linked with the occupation of the bond, and the bond strength for metallic systems), and the Laplacian of electron density, $\nabla^2\rho(\vec{r})$, at a BCP (associated with the electron depletion: the more negative $\nabla^2\rho(\vec{r})$ —the more stable the bond is).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.chemmater.3c03092>.

Tabulated lattice parameters of WCB_4 and WZrB_4 ; XRD patterns and SEM images for all ($\text{W}_{0.67}\text{Ta}_{0.33}$) C_x :4.5B and ($\text{W}_{0.92}\text{Ta}_{0.08}$) C_x :4.5B samples; Vickers hardness for all concentrations of (W_{1-x}C_x):4.5B, ($\text{W}_{1-x}\text{Si}_x$):4.5B, ($\text{W}_{0.67}\text{Ta}_{0.33}$) C_x :4.5B, and ($\text{W}_{0.92}\text{Ta}_{0.08}$) C_x :4.5B samples; representative synchrotron X-ray diffraction patterns for

WCB₄, WZrB₄, and WSiB₄; differential strain of additional lattice places (101, 110) for WB₄, WZrB₄, WCB₄, and WSiB₄; and ensemble of 3 × 2 × 1 supercell WB_{4.2} realizations (PDF)

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Notes

The authors declare the following competing financial interest(s): R.B.K. have an equity interest in SuperMetalix, Inc.

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