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# Crystal structures and formation mechanisms of boron-rich tungsten borides

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## Abstract

Boron-rich tungsten borides tend to adopt mechanically unfavorable layered structures but experimentally exhibit excellent mechanical properties rivalling traditional superhard solids. Unravelling the contra-indicated structure-property relationship, however, has been impeded by their structural ambiguities because of the difficulty in probing boron and atomic deficiency of these borides. Here we study crystal structures of boron-rich tungsten borides  $WB_{3+x}$  and  $WB_{2+x}$  by neutron diffraction based on high-quality samples prepared by a high-pressure method, leading to definitive structural resolutions for both borides with unique compositions of  $WB_{5.14}$  and  $WB_{2.34}$ . Combined with theoretical calculations, their structural stability is revealed to be closely related to atomic deficiency, which is governed by the valence-band filling with an optimal valence-electron concentration of  $\sim 10$  per cell. The presence of interstitial boron trimers at the vacant W:  $2b$  sites in  $WB_{5.14}$  alters the crystal symmetry, making the Wyckoff  $2d$  site more favorably occupied by W, rather than the  $2c$  site as previously misassigned. The staggered planar boron layers and wrinkled boron bonding in  $WB_{2.34}$  are identified to be crucial for stabilizing its structure. These findings unveil the long-standing structural mysteries of boron-rich tungsten borides and offer powerful insights for rational design of novel borides by defect chemistry.

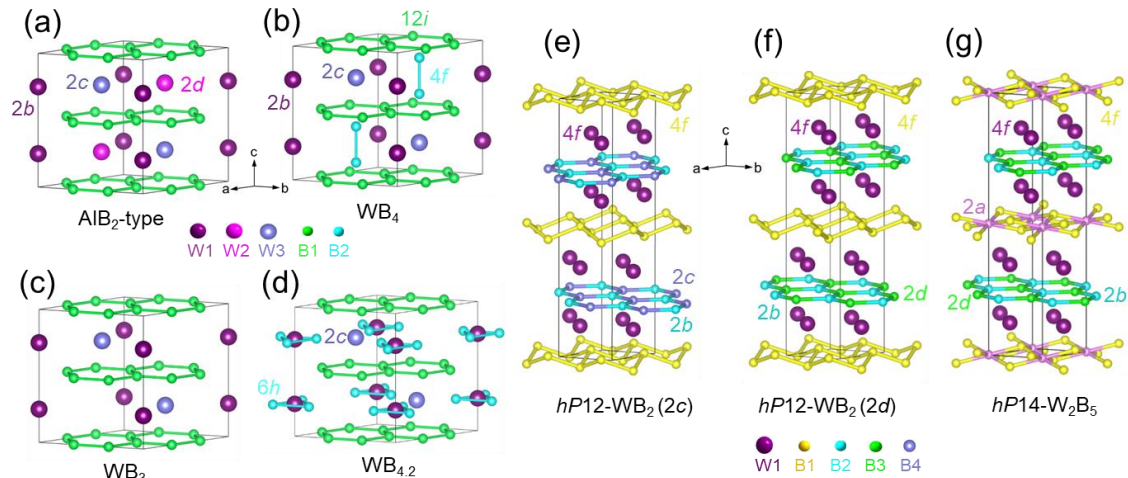
**Keywords:** *tungsten borides, neutron diffraction, high-pressure synthesis, superhard materials, atomic vacancy.*

## □. Introduction

Boron with one electron less than carbon favors forming triangular B<sub>3</sub> motif (i.e., trimer unit) with three-center bonds that can assemble into various polyhedral boron bonding networks in boron-rich solids (e.g., B<sub>6</sub>O) [1,2]. The situation is greatly changed for metal borides, because the metal can donate electrons making the electron-deficient boron more like ‘carbon’ [3], resulting in graphene-like boron nets for most metal diborides with the AlB<sub>2</sub>-type structure (Fig. 1a) [4]. However, for transition-metal (TM) diborides, such a structure becomes unstable with increasing valence electrons, leading to the formation of novel borides. Of particular interest is boron-rich tungsten borides of WB<sub>3+x</sub> (or WB<sub>4</sub>) and WB<sub>2+x</sub> (or W<sub>2</sub>B<sub>5</sub>) with superior mechanical properties rivalling those of traditional superhard solids [5-19], making them promising for practical applications as machining tools with significantly promoted efficiency over traditional carbides and superhard materials. However, their crystal structures and compositions have remained elusive for over half a century [13,20-22], impeding understanding their property-structure relationships.

The challenge for accurately determining their structures is mainly related to boron that is electron poor and nearly transparent to both x-rays and electron diffractions, in stark contrast to TM atoms that eventually dominate the overall structural factor. Although, based on x-ray diffraction (XRD) measurement, a same *P6<sub>3</sub>/mmc* symmetry was assigned for both WB<sub>3+x</sub> and WB<sub>2+x</sub> with different atomic positions and vacancies [13,20,21,23], their definitive crystal structures and compositions are still under debate. For WB<sub>3+x</sub>, WB<sub>4</sub> was initially proposed by occupying the Wyckoff *2d* site with exotic B<sub>2</sub> dimers to accommodate the experimentally-determined stoichiometry (Fig. 1b) [21]. However,

recent calculations showed that such interstitial dimers destabilize its structure [24-29], leading to a dimer-free model of  $WB_3$  (Fig. 1c) [25-30]. Although  $WB_3$  is thermodynamically stable, its structure involves a profound softening under indentation as predicted with a relatively low hardness [31], in contradiction to experiments. Besides, a few other structural models with different interstitial boron and atomic deficiencies were also proposed [13,23,32-34], but they all were quickly invalidated [18,35]. Regarding  $WB_{2+x}$ , its structure and composition are also contentious issues; conflicting reports include  $hP3$ - $WB_2$  (Fig. 1a) [36], two distinct  $hP12$ - $WB_2$  structures with differently occupied Wyckoff  $2c$  or  $2d$  site by boron (Figs. 1e-1f) [37,38],  $hP14$ - $W_2B_5$  (Fig. 1g) [20,21], and other predicted structures [28,39]. A throughout overview of  $WB_{3+x}$  and  $WB_{2+x}$  can be found in ref. [13]. Clearly, structural ambiguities of both borides cannot be clarified based on conventional x-ray-only experiments.



**Fig. 1. Possible structures for  $WB_{3+x}$  and  $WB_{2+x}$  with various compositions.** (a)  $AlB_2$ -type  $WB_2$  (i.e.,  $hP3$ ). The symmetry of the  $AlB_2$ -type structure is  $P6/mmm$  (No. 191), which can be equivalently described by  $P6_3/mmc$  (No. 194) with appropriately constrained atomic positions. (b) – (d) Possible structures of  $WB_{3+x}$ :  $WB_4$  (ref. 20),  $WB_3$  (ref. 25), and  $WB_{4.2}$  (ref. 34). (e) – (g) Possible structures of  $WB_{2+x}$ : (e)  $hP12$ - $WB_2$  ( $2c$ ) with occupied Wyckoff  $2c$  site by boron (ref. 37), (f)  $hP12$ - $WB_2$  ( $2d$ ) with occupied Wyckoff  $2d$  site by boron (ref. 36), and (g)  $hP14$ - $W_2B_5$  (i.e.,  $hP14$ - $WB_{2.5}$ ) (refs. 27 and 38). Structures in (b)-(g) have the same symmetry of  $P6_3/mmc$ .

The neutron diffraction is in this regard the best probe for determining boron (i.e., isotope  $^{11}\text{B}$ ) with a neutron scattering length even greater than that of W [40], but suffers from difficulties in preparing high-quality  $^{11}\text{B}$ -enriched sample by traditional methods because excess boron is often involved in the final products and largely exacerbates structural refinements [35]. Recently, a composition of  $\text{WB}_{4.2}$  was determined for  $\text{WB}_{3+x}$  by Lech *et al.* [35], using neutron powder diffraction (NPD) measurements based on a sample with heavy boron impurity. A prominent feature of  $\text{WB}_{4.2}$  is the randomly-distributed interstitial B3 trimers at metal-deficient sites (Fig. 1d). This structure was also lent supports from calculations using ordered orthorhombic models of  $Cmcm\text{-WB}_{4.2}$ [41] and  $Pmmn\text{-WB}_{5-x}$  [42] as structural approximates to relax the stringent requirement for computing sources; both orthorhombic phases have a same average global symmetry of  $P6_3/mmc$  to that of  $\text{WB}_{3+x}$  [41-45]. Although the Wyckoff  $2c$  and  $2d$  sites in  $\text{WB}_3$  are equivalent, they become distinguishable in  $\text{WB}_{4.2}$  because the B3 trimers have certain crystallographic orientation and alter the crystal symmetry, calling into question the adequacy of  $\text{WB}_{4.2}$  model. For  $\text{WB}_{2+x}$ , to our knowledge, no NPD data has been reported so far.

With these aims, here we formulate a high-pressure (P) route for synthesis of high-quality  $\text{WB}_{3+x}$  and  $\text{WB}_{2+x}$  samples without boron impurity for NPD experiments, leading to a definitive resolution of their structures. Mysteries of their phase stability and formation mechanism are revealed to link to an optimal filling of valence states. This work advances our understanding of the crucial role of atomic vacancies played in TM borides, which would stimulate more research efforts for discovering new borides by tailoring vacancies.

## □. Experiment details

**Sample synthesis.**  $W^{11}B_{3+x}$  and  $W^{11}B_{2+x}$  samples were prepared from the reactions between  $WCl_6$  (99.6%) and  $Na^{11}BH_4$  (99.5%) in a same molar ratio of 1:12 at 5 GPa and different temperatures (T) of 2300 and 1800 °C, respectively. Excess  $Na^{11}BH_4$  was used to establish a boron-rich environment for producing high borides of tungsten. High-P syntheses were carried out in a DS  $6 \times 10$  NM cubic press installed at the high-P lab of SUSTech with a largely extended temperature capability up to 3700 °C using our new cell assembly [46], which is very suitable for synthesis of refractory materials. Before experiment, the starting materials were homogeneously mixed and compressed into a pellet, which was then loaded in a hBN capsule and assembled with the pre-prepared cell parts for high-P synthesis. Due to the sensitivity of chloride precursor to air, all these procedures were done in a glove box with an Ar atmosphere. Both  $WB_{3+x}$  and  $WB_{2+x}$  can coexist in a wide temperature range of 2200 – 2900 °C at 5 GPa, and the addition of NaCl can largely suppress the formation of  $WB_{2+x}$ . More experimental details can be found elsewhere [46]. The recovered samples were readily purified by washing with water to remove unreacted precursors and other byproducts. For comparison,  $WB_{3+x}$  and  $WB_{2+x}$  samples were also synthesized by direct reactions of homogeneously-mixed W ( $\sim 3 \mu m$ , 99.9%) and B ( $\sim 15 \mu m$ , 99.9%) powders in molar ratios of 1:2.5 and 1:10, respectively, under the similar high P-T conditions of 5 GPa and 1800 -2600 °C. To alleviate the layer stacking faults in  $WB_{2+x}$ , it was also prepared by the reaction between  $WO_3$  and  $NaBH_4$  with a molar ratio of 1: 24 at 5 GPa and 2200 °C.

**Sample characterization.** The recovered samples were checked by an x-ray diffractometer equipped with a copper target at room temperature. Neutron diffraction

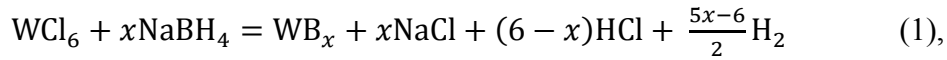
measurements were conducted at the POWGEN beamline of SNS/ORNL. Structural refinements were performed using the GSAS program [47]. The sample morphologies and microstructures were observed by the scanning electron microscopy (SEM) and transmission electron microscopy (TEM). More experimental descriptions are given in Supplemental Material [48].

**Calculations.** The calculations were carried out using the density functional theory (DFT) within the framework of Vienna *ab initio* simulation package (VASP) [49], which employs a plane-wave basis with a projector augmented wave (PAW) [50]. The generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) function was adopted as electron exchange-correlation interactions [51]. A large cutoff energy of 500 eV and dense  $k$  meshes were chosen to ensure that the total-energy calculations were converged to within 1 meV/atom. Forces on the ions were calculated through the Hellmann-Feynman theorem, allowing a full geometry optimization of structures. The formation energies ( $\Delta E$ ) of the involved metal borides were evaluated based on the relaxed structures, according to  $\Delta E(\text{TMB}_x) = E(\text{TMB}_x) - E(\text{TM}) - xE(\text{B})$ , where  $E(\text{TMB}_x)$ ,  $E(\text{TM})$ , and  $E(\text{B})$  denote the total energies of  $\text{TMB}_x$ , TM, and  $\alpha\text{-B}$ , respectively.

## □. Results and Discussion

A major disadvantage of the traditional methods for synthesizing boron-rich TM borides often involves super-excess boron in the recovered samples, as reported for  $\text{WB}_{4.2}$  and  $\text{Mo}_{0.757}\text{B}_3$  with starting TM : B ratios of 1:12 and 1:6, respectively, using arc melting and high-P methods [35,52]. Although the presence of excess boron is necessary for the suppression of other TM boride byproducts, it can hardly be separated from the final

sample and produces complex and strong NPD peaks that largely overlap with those of target material. Besides, such excess boron also contributes weak XRD peaks at high  $d$ -spacing, which would lead to misassignment of boride's symmetry, as occurred in  $WB_4$  with an initially-misassigned tetragonal structure [53]. Thus, accurately determining crystal structures of boron-rich TM borides is still challenging and many existing reports appear to be in contradiction. To settle this issue, we prepare boron-free  $WB_x$  using  $WCl_6$  and  $NaBH_4$  as starting reactants, given by

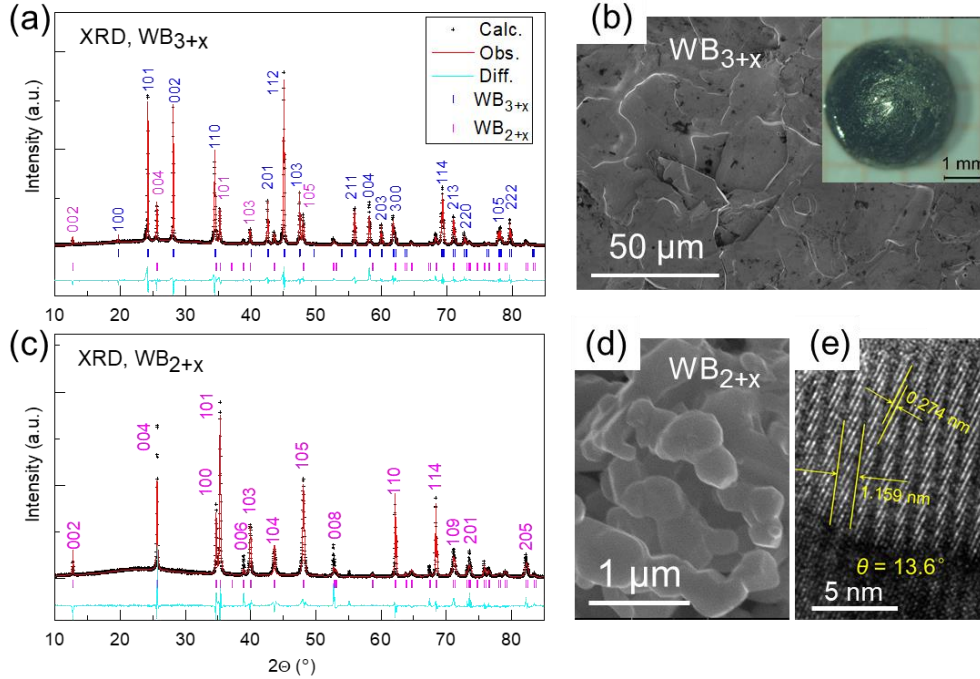


where the byproduct  $NaCl$  is identified by XRD measurement, and a sharp smell of acid released from the recovered sample suggests the presence of  $HCl$  gas. Similar reactions have been successfully used for synthesis of a number of TM diborides at ambient pressure [54-56]. Apparently, both precursors contain the highest and lowest oxidation states of  $W^{6+}$  cations and  $B^{5-}$  anions, and they are energetically more favorable for forming boron-rich borides, especially under pressure as which can effectively prompt more  $d$ -electrons of TM to participate in the chemical bonding with boron.

To obtain boron-rich borides, super-excess  $NaBH_4$  is added with a molar ratio of  $WCl_6 : NaBH_4 = 1 : 12$ . A prominent advantage of this method is that all the involved byproducts and unreacted precursors are soluble in water, which facilitates sample purification, in striking contrast to the traditional methods. As expected, the final products are high-quality boron-rich borides without involving unwanted boron (Fig. 2). For the sample synthesized at 5 GPa and 2300 °C (Fig. 2a), the recovered product is a highly dense polycrystalline bulk sample instead of well-dispersed powders, implying that it may form from a melting process (Fig. 2b). Most of the strong XRD reflection lines in Fig. 2a can be well indexed



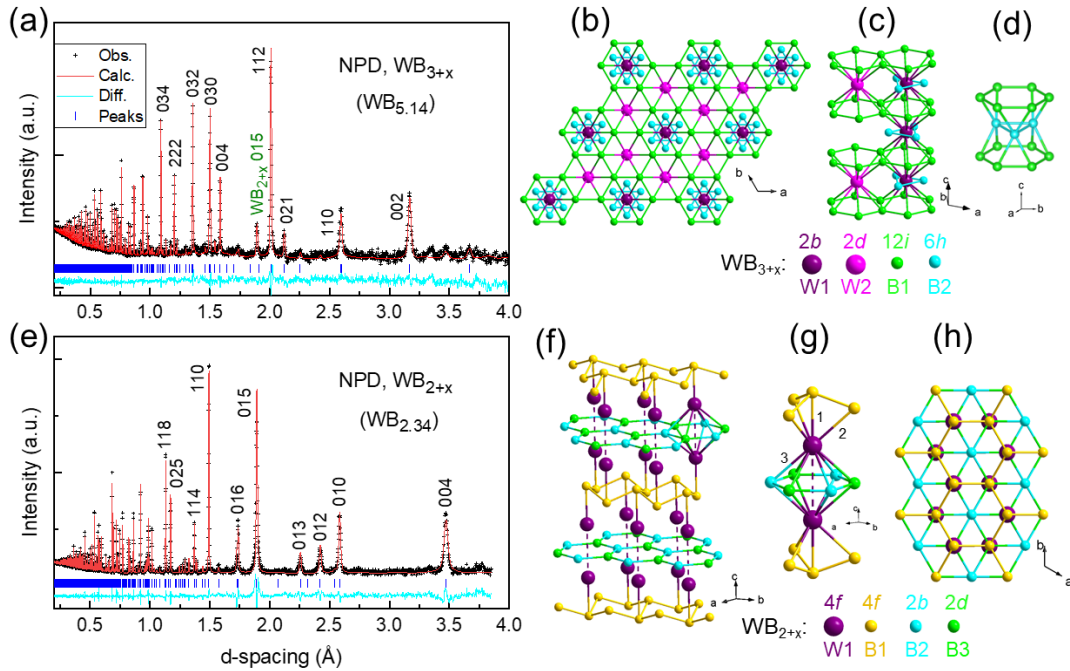
by either  $WB_3$ ,  $WB_4$ , or  $WB_{4.2}$  as they appear consistent with XRD data alone, while the remaining weak peaks can match those of the reported  $hP12-WB_2$  and  $hP14-W_2B_5$ . We find that both phases can coexist in a wide temperature range of 2200 - 2900 °C at 5 GPa.



**Fig. 2. XRD and SEM measurements of  $WB_{3+x}$  and  $WB_{2+x}$ .** (a) Refined XRD pattern for  $WB_{3+x}$  with  $WB_{2+x}$  as the only byproduct. (b) SEM image of  $WB_{3+x}$ . Inset is an optical image of bulk  $WB_{3+x}$ . (c) Refined XRD pattern for  $WB_{2+x}$ . (d) SEM image of  $WB_{2+x}$ . (e) TEM observation of Moire fringe as a result of layer stacking disorder with a layer rotation angle of  $\sim 13.6^\circ$  (Fig. S2).

As the synthesis temperature decreases,  $WB_{2+x}$  is thermodynamically more favored and its single phase can be readily obtained at 5 GPa and 1800 °C (Fig. 2c), displaying uniformly-distributed submicron grains (Fig. 2d). However, the XRD peak profile of this sample is unusual and the  $10l$  lines are anomalously broadened (e.g., 103, 104, and 105) (Fig. S1), due to the layer stacking disorder as frequently reported in layer-structured systems [57-59]. Clear Moire fringes are observed by TEM in Fig. 2e, which confirms such layer stacking disorder with an interlayer rotation angle of  $13.6^\circ$  [60] (Fig. S2) and explains the peak intensity mismatch between the simulated and observed XRD (Fig. 2c). In fact,

the similar phenomenon is also observed in the samples synthesized from the reaction between W and B at 5 GPa and 1800 °C (Fig. S3). The situation can be profoundly improved for the samples synthesized at extremely high temperature of 3000 °C or using  $\text{WO}_3$  and  $\text{NaBH}_4$  as precursors (Figs. S3-S4). Importantly, the final borides are boron free, which is beneficial to obtain high-quality NPD data.



**Fig. 3. Structural refinements for  $\text{WB}_{3+x}$  and  $\text{WB}_{2+x}$  based on neutron diffraction data taken at ambient conditions.** (a) - (c) Refined NPD pattern for  $\text{WB}_{3+x}$  and its crystal structures. (d) - (g) Refined NPD pattern for  $\text{WB}_{2+x}$  and its crystal structures. Shown in (c) and (f) is their characteristic structural units. The W-B bonds numbered with ‘1’, ‘2’, and ‘3’ have lengths of 2.235 Å, 2.341 Å, and 2.327 Å, respectively. Both samples used in the NPD measurements are the same to those in XRD experiments (Fig. 2).

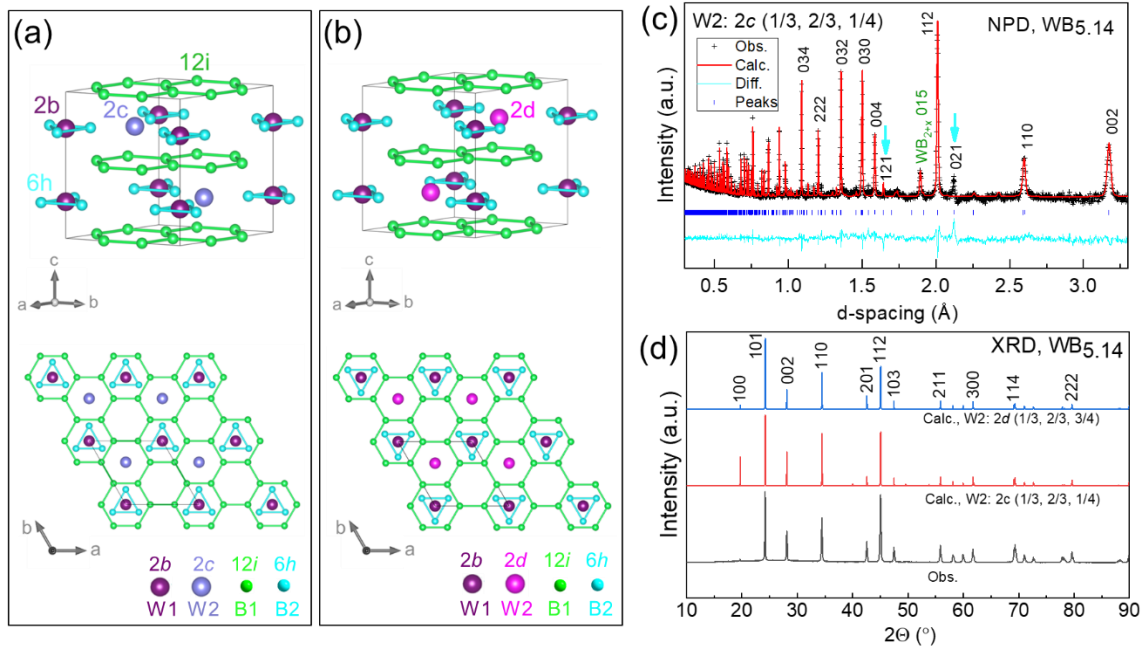
To accurately determine the crystal structures and compositions of both borides, we performed NPD measurements on high-P synthesized samples (Fig. 3), and the observed NPD profiles are significantly different from those of their XRD patterns (Fig. 2). For  $\text{WB}_{3+x}$ , a series of new and strong NPD peaks emerge including 021, 030, 032, and 034 (Fig. 3a), concurrent with the absence of 101 peak. The situation in  $\text{WB}_{2+x}$  is much more

remarkable, and its NPD pattern displays a set of almost completely different lines such as 010, 012, 013, 015, and 016 (i.e.,  $0hk$ ). Clearly, these  $0hk$  peaks only appear in the NPD pattern and should be closely associated with the boron sublattice, due to the sensitivity of  $^{11}\text{B}$  to neutron scattering with a coherent scattering length (i.e., 6.65)  $\sim 37\%$  larger than that of W (i.e., 4.86) [40]. Thus, the overall neutron scattering powers of these borides are dominated by both B and W atoms, allowing reliably extracting their structure parameters.

Using the  $\text{WB}_3$  model as an initial attempt, all the NPD reflection lines of  $\text{WB}_{3+x}$  in Fig. 3a can be indexed (Fig. S5), but with obvious discrepancies in peak intensity (e.g., 110, 021, and 032 lines), indicating the  $\text{WB}_3$  model is not adequate. Such structural inadequacy is also demonstrated in XRD pattern with a largely enhanced intensity of the 100 peak (Fig. S5), inconsistent with observations. In fact, the best refinement based on the  $\text{WB}_3$  model leads to a composition of  $\text{WB}_{4.5}$  with partially occupied W sites; however, the observed peak intensity still cannot be appropriately reproduced using such-refined  $\text{WB}_{4.5}$  (Fig. S6). Note that Wyckoff  $2c$  and  $2d$  sites in  $\text{WB}_3$  are equivalent for locating W atoms, producing the same XRD and NPD patterns (Fig. S5).

We thus attempted to refine the structure of  $\text{WB}_{3+x}$  using the  $\text{WB}_{4.2}$  model with B3 trimers (Fig. 1d and Fig. 4a). However, it is worthwhile to mention that the occupation of Wyckoff  $6h$  site with B3 trimer units lowers the symmetry of  $P6_3/mmc$ , which makes both  $2c$  and  $2d$  sites no more equivalent for being occupied by W atoms. Obviously, for the case of occupying  $2c$  site with W atoms, three vertices of the B3 trimer point to three W:  $2c$  atoms (Fig 4a), in contrast to that of the W:  $2d$  structural model with three vertices pointing to voids (Fig 4b). The former results in the absence and presence of 021 and 121 peaks (Fig. 4c), respectively, suggesting there may exist misassigned atomic positions in the

WB<sub>4.2</sub> model as recently proposed by Lech *et al.* [35]. The misassignment is likely related to W: 2c positions, because the B3 trimers in WB<sub>4.2</sub> has a specific crystallographic orientation. For both structural models, the XRD patterns are also calculated and plotted in Fig. 4d. The replacement of the 2d site with 2c site leads to a strong 100 peak, which is inconsistent with the observed. Clearly, the Wyckoff 2d is more appropriate for accommodating W atoms, rather than the 2c site, although both models can produce the nearly same composition of WB<sub>5.14</sub>. Accordingly, we replace the Wyckoff 2c site with 2d in WB<sub>4.2</sub> and apply this modified model for WB<sub>3+x</sub>, achieving an excellently refined NPD pattern (Fig. 3a and Fig. S7). The refined lattice parameters at 300 K are summarized in Table 1 and the crystal structures are depicted in Figs. 3b-3d.



**Fig. 4. Wyckoff 2c (1/3, 2/3, 1/4) vs. 2d (1/3, 2/3, 3/4) for W in WB<sub>3+x</sub> (i.e., WB<sub>5.14</sub>).** (a)-(b) Crystal structures of WB<sub>5.14</sub> with occupied 2c and 2d for W2 atoms, respectively. The bottom panel of each figure shows a different view of the crystal structure along the c-axis. (c) Refined NPD patterns for structural models in (a). (d) Calculated XRD patterns for WB<sub>5.14</sub> with two different W2 positions. In (c) and (d), Wyckoff sites for W1, B1, and B2 atoms remain invariant during calculations and refinements (see Table 1).

**Table 1.** Summary of refined lattice parameters for  $WB_{3+x}$  and  $WB_{2+x}$  based on NPD data taken at 300 K (see Fig. 3).

	$WB_{3+x}$ (300 K)		$WB_{2+x}$ (300 K)	
Formula	WB <sub>5.14</sub>		WB <sub>2.34</sub>	
System	P6 <sub>3</sub> /mmc (No. 194)		P6 <sub>3</sub> /mmc (No. 194)	
<i>a</i> , <i>c</i> [Å]	<i>a</i> = 5.2001(1), <i>c</i> = 6.3443(1)		<i>a</i> = 2.9853(2), <i>c</i> = 13.8915(2)	
Volume [Å <sup>3</sup> ]	148.5720		107.2130	
Density [g/cm <sup>3</sup> ]	7.4150		9.3126	
Atomic positions	Site	Occupancy	Site	Occupancy
	W1: 2b (0, 0, 1/4)	0.5590	W1: 4f (1/3, 2/3, 0.1375)	0.7440
	W2: 2d (1/3, 2/3, 3/4)	0.8266	B1: 4f (1/3, 2/3, 0.9766)	0.9177
	B1: 12i (0.3333, 0, 0)	1	B2: 2d (1/3, 2/3, 3/4)	1
	B2: 6h (0.1191, 0.2382, 1/4)	0.3735	B3: 2b (0, 0, 1/4)	0.6475
<i>W</i> <sub>Uiso</sub> , <i>B</i> <sub>Uiso</sub>	0.0012, 0.0020		0.0007, 0.0028	
VEC [electrons/cell]	9.88		9.69	
wR <sub>p</sub> [%], $\chi^2$	2.70, 4.23		5.43, 8.43	

The thus-refined composition of  $WB_{3+x}$  is  $WB_{5.14}$  with refined boron positions similar to those reported in ref. [35]. Compared with B: 12*i* sites that are highly occupied for forming the flat boron net, all other sites involve fractional occupations including W: 2*b*, W: 2*d*, and B: 6*h* (Table 1). The triangular B3 motif is made of B: 6*h* atoms with the center of mass located at the vacant W: 2*b* (Figs. 3b-3d), signifying an electron-deficient local environment surrounding these sites. This also suggests that both the W: 2*b* and B3 trimer cannot coexist at the same site, because the presence of metal will donate excess electrons to boron and destabilizes the trimer unit. In addition, the determined edge length of trimer is only 1.858 Å with a limited interstitial space for accommodating a big W atom. Note that the refined occupancy of B3 trimer is only 0.3735, smaller than that of W: 2*b* vacancies (i.e., 0.441), indicating that there exists ~6% voids at 2*b* sites without being occupied by either W or B3 trimer. Vacancy also occurs at W: 2*d* with an occupancy of 0.8266. Apparently, these new defective features are different from previous reports [35,42] and provide new insights into its crystal and electronic structures.

Despite a simple symmetry with a small unit cell,  $\text{WB}_{5.14}$  contains a large number of atoms, vacancies, and intricate multiautomic, which result in such intriguing composition and crystal structure made of the  $[\text{WB}_{12}]$  dumbbell building unit (Figs. 3b-3c). The partial replacement of W:  $2b$  with B3 trimer leads to a unique B15 tetradecagon unit that is randomly distributed in  $\text{WB}_{5.14}$  according to our refinement (Fig. 3d), although nonrandom W vacancies were reported in  $\text{WB}_{3+x}$  [43] and  $\text{MoB}_{3+x}$  [52]. A couple of recent theoretical studies use orthorhombic symmetries of  $Cmcm$  (No. 63) and  $Pmnm$  (No. 59) to construct pseudo-hexagonal structures for indirectly modelling  $\text{WB}_{4.2}$ -type  $\text{WB}_{3+x}$  with ordered B3 trimers. Indeed, these models can help relax stringent requirements of computing resources, allowing evaluating its phase stability and properties by calculations. The major difference between both models is the concentration of ordered B3 trimers, and our results show that  $Cmcm$ - $\text{WB}_{4.2}$  is a much better model for reproducing both the observed XRD and NPD (Figs. S8-S9).

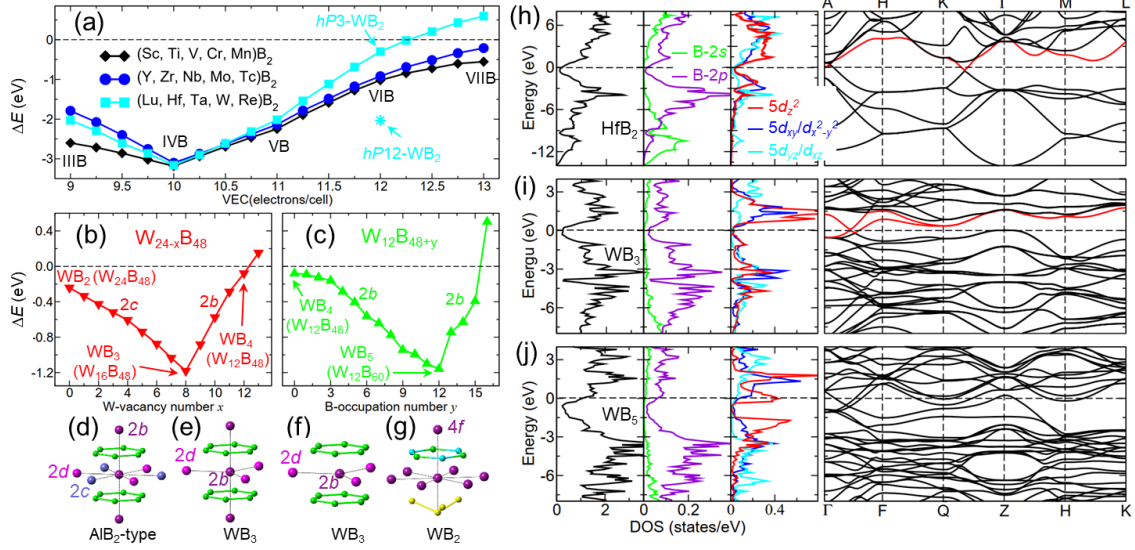
For  $\text{WB}_{2+x}$ , structural models of  $hP3$  [61] and  $hP6$  can be immediately excluded based on XRD measurements (Fig. S10), due to large mismatches between the simulated and observed XRD peaks. The models of  $hP12$ - $\text{WB}_2$  ( $2c$ ),  $hP12$ - $\text{WB}_2$  ( $2d$ ), and  $hP14$ - $\text{W}_2\text{B}_5$  produce a nearly identical XRD pattern with the observed, making them indistinguishable by the x-ray-only experiment (Fig. S10). In contrast, our NPD simulations show that  $hP12$ - $\text{WB}_2$  ( $2d$ ) (i.e., with B occupying  $2d$  site rather than  $2c$ ) is the only suitable structure for excellently reproducing the observed NPD (Fig. S11). Using this model, we performed structural refinement for  $\text{WB}_{2+x}$ , leading to a well-refined NPD pattern in Fig. 3e with slight peak intensity mismatches (e.g., 004 and 015) due to the already identified layer stacking faults (Fig. 2). The refined composition for  $\text{WB}_{2+x}$  is  $\text{WB}_{2.34}$ , close to previously reported

stoichiometry of  $\text{WB}_{2.27}$  as measured by both the wet chemical analysis and x-ray microprobe [21]. The obtained lattice parameters are listed in Table 1 and its crystal structures are illustrated in Figs. 3f-3h.

The metal interlayers of  $\text{WB}_{2.34}$  are separated and sandwiched by alternated flat and wrinkled boron sheets (Fig. 3f); thus,  $hP12\text{-WB}_{2+x}$  is an intermediate between  $\text{AlB}_2$ - and  $\text{ReB}_2$ -type phases (Fig. S10). Puckering of the flat B sheets is probably induced by excess electrons as denoted by metal [4]. A relative in-plane shift of the wrinkled boron sheets causes overlap of the associated B and W atoms along the  $c$ -axis (Figs. 3f-3h), resulting in three different W-B bond lengths of 2.235 Å, 2.341 Å, and 2.327 Å, a slightly shorter than that of 2.348 Å in  $\text{WB}_{5.14}$ . The shortest bond (i.e., 2.235 Å) is formed between W and B of the adjacent wrinkled sheet along the  $c$ -axis through a strong hybridization of W:  $5d_z^2$  and B:  $p_z$  orbitals, which is crucial for stabilizing the  $hP12$  structure.

Similar to  $\text{WB}_{5.14}$ ,  $\text{WB}_{2.34}$  also has complicated fractional atomic occupations (Table 1). The obtained vacancy fractions in the W-W layer and wrinkled B sheet are ~26% and 8%, respectively. Contrary to what one might expect, both B:  $2b$  and  $2d$  sites possess largely different vacancies, although they come from the same planar B sheet, signaling nonrandom vacancies in the planar B sheet. This occupation disparity between  $2b$  and  $2d$  sites is likely due to their different local bonding states. Obviously, no boron atom from the adjacent wrinkled B sheets can overlap with B:  $2b$  atoms along the  $c$ -axis, in contrast to that of B:  $2d$  atoms. Most intriguingly, both  $\text{WB}_{5.14}$  and  $\text{WB}_{2.34}$  have a nearly same valence-electron concentration (VEC) of ~10 per cell (Table 1), indicating a similar electronic mechanism for governing their structural stabilities. Besides, no phase transition is observed in both borides at low temperatures (Fig. S12); we also refined their structures

and compositions at 7 K (Table S1) with results similar to the cases at 300 K.



**Fig. 5.** Calculated formation energies ( $\Delta E$ ), density of states (DOS), and electronic band structures for TM borides. (a)  $\Delta E$  vs. VEC for  $3d$ -,  $4d$ - and  $5d$ -TMB<sub>2</sub>. Borides with fractional VEC values (e.g., 9.25, 9.5, and 9.75) can be formed by containing both the nearest neighboring metals in different molar ratios of 3:1, 1:1, and 1:3 (e.g., (Sc<sub>0.75</sub>Ti<sub>0.25</sub>)B<sub>2</sub>, (Sc<sub>0.5</sub>Ti<sub>0.5</sub>)B<sub>2</sub>, and (Sc<sub>0.25</sub>Ti<sub>0.75</sub>)B<sub>2</sub>). (b)  $\Delta E$  vs. metal vacancy ( $x$ ) at the Wyckoff  $2c$  ( $1/3$ ,  $2/3$ ,  $1/4$ ) (i.e.,  $x = 0 - 8$ ) and  $2b$  ( $0$ ,  $0$ ,  $1/4$ ) (i.e.,  $x = 8 - 13$ ) for the AlB<sub>2</sub>-type  $W_{24-x}B_{48}$  supercell (see Fig. 1a). (c)  $\Delta E$  vs. occupation of excess boron ( $y$ ) at the Wyckoff  $6h$  ( $x$ ,  $2x$ ,  $1/4$ ) for the  $W_{12}B_{48+y}$  supercell with a metal-deficient AlB<sub>2</sub>-type structure (i.e., the  $2c$  and  $2b$  sites are fully and half unoccupied by W, respectively). All energies are rescaled for one TMB <sub>$x$</sub>  formula in a primitive cell. (d)–(g) Structural units for *hP3*-WB<sub>2</sub>, WB<sub>3</sub>, and *hP12*-WB<sub>2</sub>. (h)–(j) Total and partially projected DOS and band structures for HfB<sub>2</sub>, WB<sub>3</sub>, and WB<sub>5</sub>. The Fermi levels at 0 eV are denoted with horizontal dashed lines.

To explore the underlying formation mechanisms for both borides, we systematically evaluated the formation energy for *hP3*-diborides of  $3d$ -,  $4d$ - and  $5d$ -TM series to establish the relation of structural stability and VEC (Fig. 5). The calculated energies for these *hP3*-TMB<sub>2</sub> series have a similar trend as the VEC varies (Fig. 5a); a global minimum occurs at an optimal value of 10 per cell for achieving the highest stability (e.g., TiB<sub>2</sub>). However, *hP3*-WB<sub>2</sub> possesses a VEC of 12 per cell with a large formation energy, accounting for its instability. By contrast, *hP12*-WB<sub>2</sub> with staggered and wrinkled boron sheets is thermodynamically more favorable with a dramatically-reduced formation energy (Fig. 5a).



In fact,  $WB_{5.14}$  can be viewed as a structural derivative of  $hP3-WB_2$  by introducing metal vacancies and boron trimers, as demonstrated in Fig. 1. Thus, we construct a  $hP3$  supercell of  $W_{24-x}B_{48+y}$  and calculate its formation energy with varying  $x$  and  $y$  to evaluate its stability. As expected, the increase of vacancy at W:  $2c$  gradually decreases the formation energy of  $W_{24-x}B_{48}$  (Fig. 5b), achieving a valley value at  $x = 8$  that corresponds to the ideal  $WB_3$  model with fully unoccupied  $2c$ . Before adding interstitial B3 trimer, we continue taking W out of the structure from the  $2b$  site, leading to the increase of formation energy. To accommodate the refined occupancy of W:  $2b$  (i.e.,  $\sim 0.5$ ) (Table 1), half W:  $2b$  atoms are randomly removed and results in an unstable phase  $WB_4$  at  $x = 12$  with a higher energy. Filling the vacant W:  $2b$  in  $WB_4$  (i.e.,  $W_{12}B_{48+y}$ ) with B atoms as an approximate replacement for boron trimer rapidly lowers its formation energy (Fig. 5c); an energy valley is reached when twelve B are added (i.e.,  $y = 12$ ), followed by an increase of energy with adding more B atoms. Obviously, the most stable composition  $WB_5$  (i.e.,  $W_{12}B_{60}$ ) occurs at the bottom of the valley, excellently rationalizing our refined  $WB_{5.14}$ . Besides, the added twelve B atoms in  $WB_5$  are randomly distributed in four vacant W:  $2b$  sites with an average occupation number of 3, equivalent to the filling of a B3 trimer at each site.

To gain insights into their formation mechanisms, we explored electronic properties of the associated borides with key structural units shown in Figs. 5d-5g. By contrast to the  $AlB_2$ -type structure (Fig. 5d), the absence of W:  $2c$  in  $WB_3$  forms honeycomb W layers that are alternately stacked with planar B sheets in two distinct stacking modes (Figs. 5e-5f and Fig. S13-S14). A relative shift of the wrinkled B sheet in  $hP12-WB_2$  leads to a new bonding sequence of B-W-W along the  $c$ -axis (Fig. 5g). Using  $hP3-HfB_2$  with an optimal VEC of 10 per cell as an illustrative case, we calculated its electronic band structure and

density of states (DOS) and plotted in Fig. 5h, showing a significant overlap of the states from metal and B with a Fermi level pinned at the bottom of a pseudogap, indicating a strong metal-B bonding. Below the Fermi level, the bonding states contain five degenerated bands and can be grouped into two groups of high- and low-energy bands, which are formed by hybridizations of  $5d_{xy}$ ,  $5d_{x^2-y^2}$  and B:  $2p_{x/y}$  and of  $5d_{yz}$ ,  $5d_{xz}$  and nonbonding B:  $2p_z$  states, respectively. Apparently, such five bands are capable of being filled with a maximum VEC of 10 per cell, which explains the reason why *hP3*-diborides have an optimal VEC of 10 per cell (Fig. 5a). Further increase of VEC will cause the filling of  $5d_{z^2}$  in the antibonding band above the Fermi level. However, the  $5d_{z^2}$  orbital is linked to the direct TM-TM interaction along the *c*-axis, perpendicular to the B layers (Fig. 5d), and hence destabilizes the *hP3* phase. Thus, instability of *hP3*-WB<sub>2</sub> results from fully occupied  $5d_{z^2}$  states.

Removing the W:  $2c$  atoms from *hP3*-WB<sub>2</sub> creates WB<sub>3</sub> with an optimal VEC of 10 (Fig. 5i), satisfying the criterion for forming a stable phase with calculated DOS and band structures resembling those of HfB<sub>2</sub>. In WB<sub>3</sub>, the  $5d_{z^2}$  states of W:  $2b$  atoms are completely depleted in Fig. 5f, while those in Fig. 5e should be partially filled due to the existence of strong W-W repulsions along the *c*-axis [4], as also indicated by a slightly occupied  $5d_{z^2}$  band across the Fermi level (Fig. 5i). Over-filling of such unfavorable  $5d_{z^2}$  states would induce structural instability, hence the occurrence of vacant W:  $2b$  to reduce VEC for achieving a stable state. On the other hand, if the bonding bands below the Fermi level are less filled, the system will also become unstable with increased formation energy, as occurred in WB<sub>4</sub> with only half-filled W:  $2b$  (Fig. 5b). The insertion of B<sub>3</sub> trimers at the vacant W:  $2b$  compensates the reduction of VEC for the formation of WB<sub>5</sub>; coupling of the

trimer and two adjacent B layers produces a key structural unit of B15 tetradecagon that can sufficiently strengthen its structure and mechanical properties [41]. The calculated DOS and band structure for WB<sub>5</sub> are similar to those of WB<sub>3</sub> with strongly overlapped and hybridized bonding states between W and B, giving rise to a broad pseudogap around the Fermi level (Fig. 5j). These properties further confirm that WB<sub>5</sub> is an energetically favorable phase.

Staggering the boron sheets of *hP3*-WB<sub>2</sub> provides an alternative approach to relieve the filling of unfavorable antibonding state of  $5d_{z^2}$  by transferring electrons to the  $5d_{z^2}$ -B:  $p_z$  bonding band (Fig. 5g), leading to the puckering of staggered B sheets, similar to the observed in ReB<sub>2</sub> [4]. As a result, *hP12*-WB<sub>2</sub> is formed with a sharp reduction of the formation energy (Fig. 5a), although it has a large VEC of 12 per cell. However, our experiments showed that only defective *hP12*-WB<sub>2</sub> can be synthesized with a realistic composition of WB<sub>2.34</sub>. Interestingly, the VEC value of WB<sub>2.34</sub> is 9.69 close to 10 per cell, suggesting its phase stability should also be dictated by a similar electronic mechanism. Further theoretical work on WB<sub>2.34</sub> is warranted for exploring its electronic properties and the crucial role of vacancies played in this material by calculations.

## □. Conclusions

In summary, we have formulated a high-P method for the synthesis of boron-free WB<sub>3+x</sub> and WB<sub>2+x</sub> samples. Based on these samples, high-quality neutron diffraction data are collected and refined for solving their long-standing structural ambiguities. The determined compositions for both borides are WB<sub>5.14</sub> and WB<sub>2.34</sub> with a similar VEC of ~10 per cell, obeying our established criterion for the formation of stable hexagonal boron-rich borides.

A number of previously unidentified structural features are also unveiled for both compounds, including the misassigned W: 2c site in  $WB_{3+x}$  and unique atomic deficiencies in  $WB_{2+x}$ . Our findings offer powerful insights into the electronic origin of atomic vacancies in boron-rich borides, which is crucial for understanding their structural stability and formation mechanism. The definitively resolved crystal structures for both borides would provide important foundations for study of their structure-property relationships and for rational design of new borides with enhanced properties by tailoring crystalline defects.

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### Data availability

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

### Competing interests

The authors declare no competing interests.

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