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Effect of Defects in the Formation of AlB_2-Type WB_2 and MoB_2

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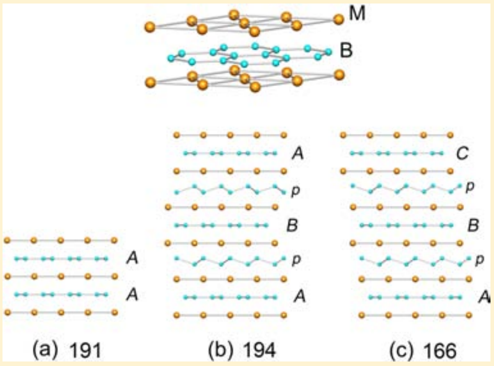
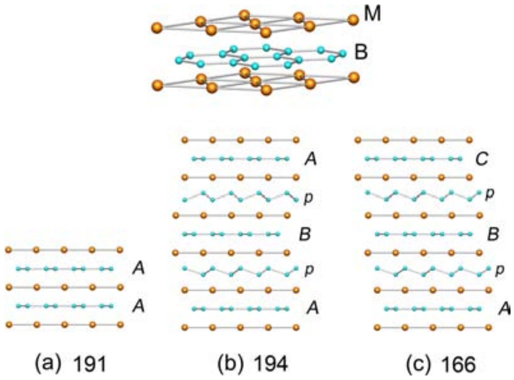
ABSTRACT: Tungsten diboride, WB_2, usually has a hexagonal structure with the space group $P6_3/mmc$ (number 194); and molybdenum diboride, MoB_2, has a trigonal structure with $R\bar{3}m$ (number 166). Other than these phases, both diborides are reported to have a phase with an AlB_2-type structure ($P6/mmm$, number 191). AlB_2-type MoB_2 is easy to synthesize and has been extensively studied, whereas AlB_2-type WB_2 is very difficult to synthesize and has appeared only once in a report by Woods et al. in 1966 (Woods, H. P.; Wawner, Jr., F. E.; Fox, B. G. *Science* **1966**, *151*, 75.) We have investigated these diborides by means of first-principles calculations and found that boron defects are responsible for the difference in their synthesizability. AlB_2-type MoB_2 became stable enough with some boron defects added, while AlB_2-type WB_2 became minimally stable, suggesting it may not actually exist. Following our calculations, we attempted to synthesize AlB_2-type WB_2 with the optimum quantity of boron defects but observed no trace of it. We conclude, from both calculations and experiments, that AlB_2-type WB_2 does not exist stably in the W−B phase diagram and that the compound produced in Woods et al.'s report might have contained some impurities.



INTRODUCTION

Boron, a light element in group 13, has a chemical nature that more closely resembles C and Si than that of Al and Ga in the same group. Boron combines with most metallic elements except the noble metals, yielding a variety of metal-rich and boron-rich borides.[2] Diborides of group 2, 3, 4, and 5 metals (MB_2) have an AlB_2-type structure, as illustrated at the top of Figure 1, in which M atoms form layers of hexagonal lattices and B atoms form graphitic layers between them. A side view is presented in Figure 1a. Its space group is $P6/mmm$ (number 191). Of the group 6 metals, CrB_2 has only an AlB_2 structure,[3] while MoB_2 and WB_2 have AlB_2 and other structures. The main phase of WB_2 is illustrated in Figure 1b, in which AlB_2 units (*A* and *B*) are periodically stacked along the *c* axis with cyclohexane-like puckered B layers (*p*). This structure was first determined by Kiessling as W_2B_5.[4] It was later confirmed that one boron atom is absent, and the stoichiometric composition is WB_2,[5−9] with a space group of $P6_3/mmc$ (number 194). In the same way, the main phase of MoB_2 (Figure 1c) has AlB_2 units (*A*, *B*, *C*) stacked with puckered B layers. It was first assumed to be Mo_2B_5[4] and later confirmed to be MoB_2.[6,7,9] The space group is $R\bar{3}m$ (number 166). Hereinafter we refer to these three phases by adding a space group number to each material: for example, WB_2-191. There have, so far, been reports on MoB_2-191,[9−11] MoB_2-166,[4,6,7,9,11] WB_2-191,[1] WB_2-194,[4−6,8,9,12,13] and WB_2-166.[14]



(a) 191 (b) 194 (c) 166

Figure 1. AlB_2-type structure (top) and three derivative structures. *A*, *B*, and *C* denote AlB_2-type layers and *p* denotes a puckered boron layer. Numbers denote space group numbers.

There are reports on the synthesis of MoB_2-191 (AlB_2-type), and its region of stability in the Mo−B phase diagram has been determined.[15−17] However, there is only one report on the synthesis of WB_2-191, by Woods et al. in 1966.[1] This synthesis has not since been reproduced,[4−6,8,9,12,13] and some people are skeptical of its existence. Frotscher et al. calculated, from first principles, the total energies of the three phases of WB_2 and found that the 191 phase has about 0.7 eV higher energy than the other two phases.[9] They also synthesized WB_2 and observed no traces of the 191 phase. Zhao et al. also calculated the total energies of WB_2 and other tungsten borides and arrived at almost the same result as Frotscher's.[18] They calculated the enthalpies under high pressure and showed that WB_2-191 would be more stable than WB_2-194 at over 90 GP.

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Table 1. Calculated Lattice Constants and Relative Total Energies Per Formula Unit (f.u.) of WB_2 and MoB_2[a]

phase	a (Å)	c (Å)	relative total energy/f.u. (eV)
WB_2-191	2.9721 (3.02[b])	3.5838 (3.05)	0.669
WB_2-194	3.0379 (2.9822[c])	14.1231 (13.8741)	0
WB_2-166	3.0310 (3.011[d])	21.3050 (20.93)	0.006
MoB_2-191	2.9863 (3.043[e])	3.5489 (3.067)	0.362
MoB_2-194	3.0410 (−)	14.0972 (−)	0.001
MoB_2-166	3.0405 (3.0138[e])	21.2152 (20.9541)	0

[a] Experimental values are in parentheses. Total energies are relative to WB_2-194 and MoB_2-166, respectively. [b] Reference 1. [c] Reference 8. [d] Reference 14. [e] Reference 9.

In the present study, our intention is to clarify from first-principles calculations why WB_2-191 is more difficult to synthesize than MoB_2-191 and discuss whether the result by Woods et al. for WB_2-191 is likely to be true. We examined in particular the influence of boron defects in these materials on the lattice constants, the total energies, and the electron densities of states, since boron defects are necessarily included in real MoB_2-191 (and WB_2-191, probably) but were not considered in previous studies.[9,18] Following these calculations, we attempted an experiment to synthesize WB_2-191 that included defects.

■ COMPUTATIONAL METHODS

The calculations of the total energies were carried out with full optimization of lattice constants and geometries within hexagonal symmetry. We used CPMD code, version 3.13.2,[19−21] which is based on the density functional theory with plane waves and pseudopotentials.[22,23] Norm-conserving Troullier-Martins-type pseudopotentials[24] in the Kleinman-Bylander form were used.[25] The generalized gradient approximation (GGA) was included by means of the functional derived by Becke[26] and by Lee, Yang, and Parr.[27] An energy cutoff of 50 Ry was sufficient to provide a convergence for total energies and geometries. The calculations were done using Monkhorst-Pack sampling[28] of an (8 × 8 × 8) mesh for the 191 phase and an (8 × 8 × 2) mesh for the 194 and 166 phases. A test calculation for the 191 phase with a (12 × 12 × 12) mesh was compared, which showed the difference in total energy per unit cell of about 1 meV.

■ RESULTS AND DISCUSSION

The calculated lattice constants and relative total energies per formula unit (f.u.) are summarized in Table 1. The total energies are relative to the most stable phase of each material, WB_2-194 and MoB_2-166, respectively. The lattice constants are in good agreement with the experimental values in the parentheses except for WB_2-191 and MoB_2-191. There have been no experimental reports on MoB_2-194. The fact that the calculated c values for both 191 phases deviate by as much as 15% from the experimental values indicates that neither of the 191 phases can be synthesized with this composition (no boron defects). This is also confirmed by their total energies. WB_2-191 has 0.669 eV higher energy than WB_2-194, which agrees closely with the previous studies,[9,18] and similarly MoB_2-191 has 0.362 eV higher energy than MoB_2-166. The energy difference for WB_2-191 is about double that of MoB_2-191, suggesting that WB_2-191 is more difficult to synthesize than MoB_2-191.

The total energy differences between the 194 and 166 phases are very small for both materials because their structures are almost identical except for how they are stacked (Figure 1). WB_2-194 has slightly lower energy than WB_2-166 (by 0.006 eV), and MoB_2-194 conversely has a higher energy than MoB_2-166 (by 0.001 eV). This agrees with the experimental fact that WB_2 prefers the 194 phase to the 166 phase, and MoB_2 prefers the 166 phase to the 194 phase. Frotscher et al.[9] reports that WB_2-166 has a slightly lower energy than WB_2-194, which is contrary to our results. This small difference in energy is likely attributable to the GGA, which was included in our calculations but not in theirs.

The reason that the 191 phases have a high total energy and are unstable can be qualitatively explained in terms of their electron densities of states (DOS), shown in Figure 2. For the stable phases, WB_2-194 and MoB_2-166 (dashed lines), a pseudo gap is observed at around −1.3 eV. The states below the pseudo gap have a bonding nature and those above the gap have an antibonding nature, which was confirmed from gap widening under high pressure. Both phases have several occupied antibonding states, since the Fermi level lies above the pseudo gap. On the other hand, WB_2-191 and MoB_2-191 (solid lines) have a pseudo gap at around −2.0 to −2.2 eV. This means that both 191 phases have a somewhat higher Fermi level than WB_2-194 and MoB_2-166. In addition, the 191 phases have about double the peak height around the Fermi level as WB_2-194 and MoB_2-166. These features cause the 191 phases to have more antibonding electrons and to be less stable than WB_2-194 and MoB_2-166.

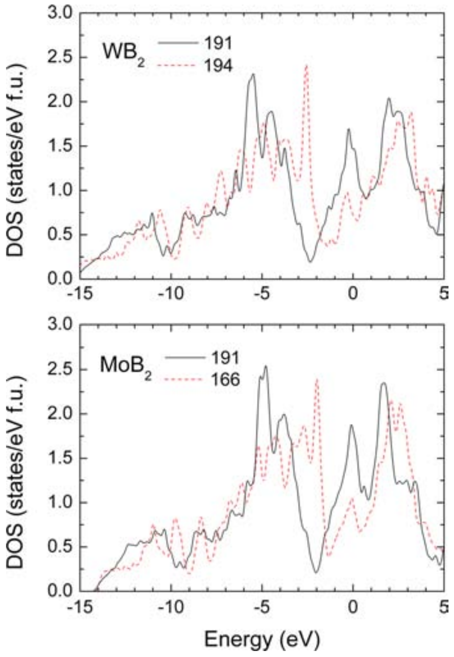

Figure 2. Electron densities of states of WB_2-191, -194 (top) and MoB_2-191, -166 (bottom).

Up to this point, we have examined the possibility of the 191 phases, which we assume have no boron defects. MoB_2-191 can be experimentally synthesized only if it has some B defects.[9,15,16] Since the electronic structures of MoB_2-191 and WB_2-191 are similar, WB_2-191, if it really exists, is likely to have B defects. We thereby examined the defect dependence of the lattice constants and the total energy of the 191 phases. We considered a (2 × 2 × 2) supercell for calculation of the 191 phase. The supercell has 16 B atoms, and from one to three B atoms were removed, corresponding to $x = 0.125$ to 0.375 in the formula $Mo(W)B_{2-x}$. There are several ways to remove two and three B atoms from the supercell. The total energy was the highest when two adjacent B atoms were removed and the lowest when two B defects were arranged as in Figure 3 (left), in which defects are indicated in dark blue. Figure 3 (right) shows the lowest-energy configuration of three B defects. When four or more B atoms were removed ($x > 0.5$), the electronic structures did not reach convergence, suggesting the 191 phases were now unstable.

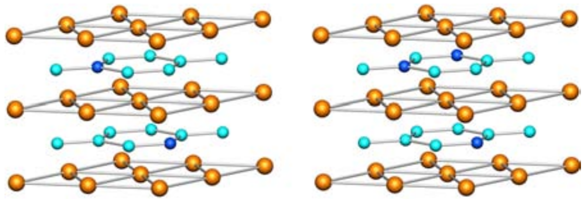

Figure 3. Configurations of boron defects in the 191-phase supercell. Dark blue spheres denote defects.

The lattice constants of the 191 phases as a function of x, the amount of B defects, are shown in Figure 4. The closed circles and triangles denote the c and a of WB_{2-x}, and the open circles and triangles denote those of MoB_{2-x}. Both phases show similar behavior. When x increases from 0 to 0.375, the c values decrease by as much as 15% and the a values increase slightly, by about 3%, with the result that a and c values closely approach each other. At $x = 0.375$, they are $a = 3.072$ and $c = 3.117$ Å for WB_{2-x} and $a = 3.077$ and $c = 3.109$ Å for MoB_{2-x}. These values for MoB_{2-x} agree closely with the experimental values for MoB_2-191, $a = 3.043$ and $c = 3.067$ Å, which is to be expected because MoB_2-191 is synthesized with B defects.[9] It must be noted that the lattice constants of WB_2-191, as reported by Woods et al. ($a = 3.02$, $c = 3.05$ Å),[1] also agree closely with the calculated values. This agreement suggests that the sample they synthesized was likely to include B defects, though they did not mention it. The agreement of the lattice constants, however, is not sufficient to prove the existence of WB_2-191, so it must be judged in terms of its relative total energy to other phases.

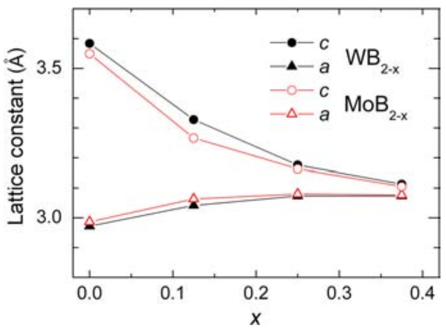

Figure 4. Defect dependences of the lattice constants of WB_{2-x}-191 (black filled circles and triangles) and MoB_{2-x}-191 (red open circles and triangles).

In the experimental phase diagram of the W−B binary system (Figure 5 top),[29,30] WB_{2-x} ($x = 0-1$) decomposes into tungsten monoboride, WB, and WB_2-194 and can be expressed as

$$WB_{2-x}\text{-}191 = x\text{WB} + (1 - x)WB_2\text{-}194 \tag{1}$$

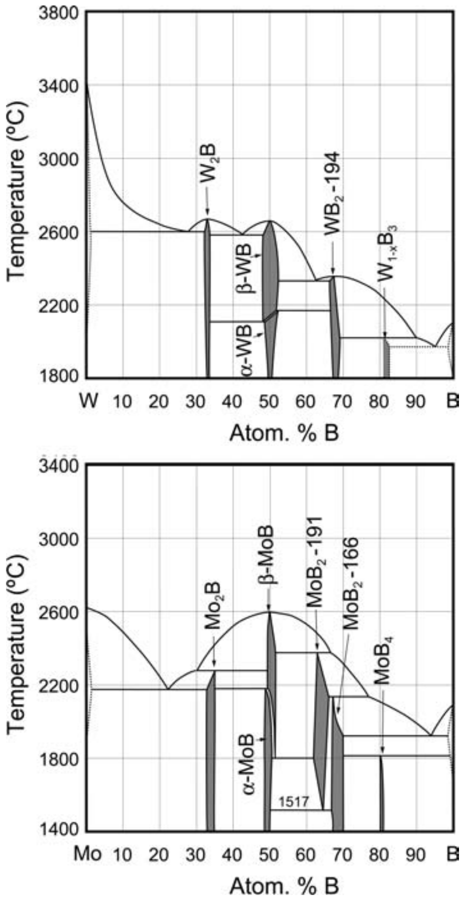

Figure 5. Phase diagrams of W−B and Mo−B binary systems.

The numbers of W and B atoms are equal on both sides. There are two phases for WB, α and β, and here we deal with the low-temperature α phase, which has a lower energy. This equation is designed to estimate the difference in the total energy between the left and the right sides, so that it does not assume the actual existence of WB_2-191. Similarly, MoB_{2-x}-191 is expressed as a sum of MoB (α phase) and MoB_2-166 as

$$MoB_{2-x}\text{-}191 = x\text{MoB} + (1 - x)MoB_2\text{-}166 \tag{2}$$

MoB_{2-x}-191 exists stably in the Mo−B phase diagram at above 1517 °C (1790 K) (Figure 5 bottom).[15−17]

The differences in total energy of the left side from that of the right side in eqs 1 and 2 are plotted in Figure 6 as a function of x. When $x = 0$ (no defects), the energy difference of WB_{2-x}-191 is 0.669 eV, which is the same as that shown in Table 1. As defects increase in number, the energy difference decreases and becomes slightly negative near $x = 0.35$ when the left side of eq 1, WB_{2-x}-191, becomes stable. With one more B atom removed ($x = 0.5$), the calculation did not converge, suggesting that WB_{2-x}-191 becomes unstable. Thus, the region of x in which

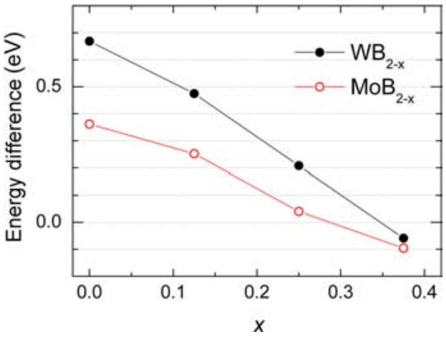

Figure 6. Total energy differences of WB_{2-x}-191 (black filled circles) and MoB_{2-x}-191 (red open circles). The differences are between the left sides and the right sides in eqs 1 and 2.

WB_{2-x}-191 is more stable than (WB + WB_2-194) is very narrow, and the energy difference, about −0.059 eV at x = 0.375, is small. This explains why WB_{2-x}-191 is difficult to synthesize, and it is unclear if WB_{2-x}-191 can really be stable in experiments, since the free energy generated by defects and phonons at finite temperature is not included in the calculations. On the other hand, the energy difference of MoB_{2-x}-191 with no defects is 0.36 eV, about half of that of WB_{2-x}-191, and it becomes negative at a lower x (about 0.29) than that for WB_{2-x}-191. This means that the region of x in which MoB_{2-x}-191 is more stable than (MoB + MoB_2-166) is wider than that of WB_{2-x}-191. In addition, the minimum energy, −0.096 eV (x = 0.375), is 1.63 times as low as that of WB_{2-x}-191. These facts explain why MoB_{2-x}-191 is easier to synthesize.

In general, the total energies of two different systems cannot be compared. However, in the present case, we can expect eqs 1 and 2 to be comparable for the following reasons: (i) Both W and Mo are group 6 elements and their chemical characteristics are similar. (ii) Their pseudopotentials are constructed in the same manner. (iii) WB_{2-x}-191 and MoB_{2-x}-191 have the same crystal structure, as do WB and MoB. WB_2-194 and MoB_2-166 have almost the same crystal structure except how the atomic layers are stacked. Since most of the calculation errors arise from pseudopotentials and k-point sampling that varies according to crystal symmetry, eqs 1 and 2 are expected to be subject to the same pattern of calculation errors and thus are comparable. This is, of course, an empirical assumption. We therefore carried out an experiment to confirm our calculations as shown later in this section.

How B defects stabilize the 191 phases is seen in their DOSs (Figure 7). The Fermi level is set at 0 eV. Both DOSs are similar to each other. Without defects (x = 0, solid line), the Fermi levels are at about 2 eV higher than the pseudo gap. As mentioned in Figure 2, states higher than the pseudo gap have an antibonding nature, making the 191 phases less stable than the other phases. With as many defects as possible (x = 0.375, dashed line), the Fermi levels shift to around the bottom of the pseudo gap while the DOSs maintain their overall shapes. The electrons with antibonding nature accordingly decrease and the 191 phases are stabilized. If more defects were added, the electrons with bonding nature would decrease, making the 191 phases less stable than at x = 0.375.

Our calculations indicate that MoB_{2-x}-191 is stable at 0 K. However, in the Mo−B phase diagram (Figure 5), MoB_{2-x}-191 exists at not lower than 1517 °C (1790 K). This discrepancy is attributable to the error in the total energy calculations based on eqs 1 and 2. The materials on the left- and right-hand sides have different shapes and sizes of unit cells, so a comparison of the total energies inevitably involves some error. In spite of this, its variation with x, the amount of defects, is reliable, since most of the errors are canceled out. In fact, the composition of MoB_{2-x}-191 at 1517 °C is $MoB_{1.62}$, corresponding to x = 0.38, which agrees closely with our result. When the temperature increases, the region of x for MoB_{2-x}-191 widens, probably because its free energy falls somewhat due to the entropy from the phonons and the configurations of the defects.

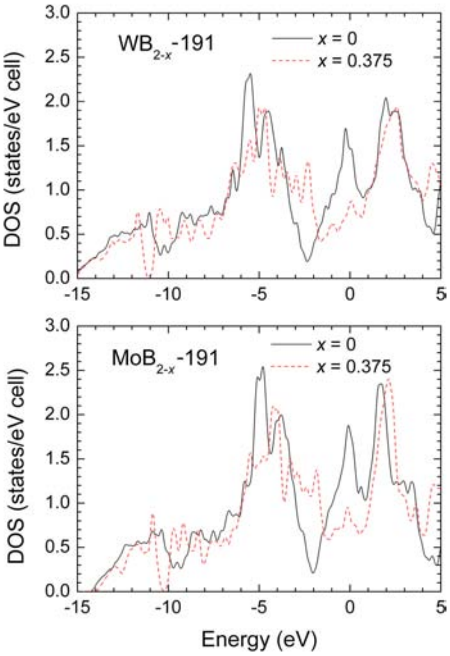

Figure 7. Electron densities of states of WB_{2-x}-191 (top) and MoB_{2-x}-191 (bottom). Solid lines (black), x = 0; dashed lines (red), x = 0.375.

Judging from the case of MoB_{2-x}-191, it is not easy to decide whether WB_{2-x}-191 actually exists, since from our calculations, WB_{2-x}-191 is minimally stable under the optimal condition of x = 0.375. Assuming that the calculation errors show the same tendency in MoB_{2-x} and WB_{2-x}, WB_{2-x}-191 must be synthesized in a high-temperature region if it exists. To investigate the likelihood of WB_{2-x}-191 existing, we made an attempt to synthesize WB_{2-x}-191 at a high temperature below its melting point.

A sample rod was prepared by mixing commercially available powders of WB_2-194 and W, adjusting the B/W ratio to 1.62, which our calculations suggest is likely to be the most stable composition and is an analogue of MoB_{2-x}-191 (x = 0.38). The rod was formed by isostatic pressing and then sintered at 1500 °C under vacuum. The rod was melted using the floating zone method in an Ar atmosphere and rapidly cooled to prevent any transformation to low-temperature phases. The part of the sample that solidified first was then investigated by powder X-ray diffraction. We observed diffraction peaks for WB_2-194 and WB but none for WB_{2-x}-191. If WB_{2-x}-191 exists, it should appear in the compounds, even if the composition x deviates slightly from the optimum value. We thus conclude that the WB_{2-x}-191 phase does not exist stably in the W−B binary system.

We now review the report on WB_2-191 by Woods et al.[1] in the light of our calculations and experiments. If the compound they obtained was the true 191 phase, it was in a metastable state rather than in a stable state. In this case, it must have contained boron defects and the composition was probably close to $WB_{1.62}$ since their compound had lattice constants close to our calculated values for WB_{2-x}-191 (x = 0.375) (Figure 4).

There are, however, some questions surrounding their experiment. First, the synthesis temperature was 800 °C (1073 K), much lower than that for MoB_{2-x}-191 which was 1517 °C (1790 K) (Figure 5). Since WB_{2-x}-191 has a higher relative energy than MoB_{2-x}-191 (Figure 6), we would expect WB_{2-x}-191 to be synthesized at a higher temperature than MoB_{2-x}-191. Second, their experiment employed chemical vapor deposition, in which a heated boron fiber was exposed to flowing WCl_6 gas. The region of stability of x for WB_{2-x}-191 is very narrow (Figure 6), and it is not evident how their sample could have had this optimum composition.

These facts suggest that their sample might have included impurities. It is conceivable that the boron fiber or WCl_6 gas contained some impurities, or the degree of vacuum might not have been satisfactory. There are examples in which impurities such as C and N stabilize the boron phase (α-tetragonal) that would be unstable without their presence.[31−33]

The morphology of their sample was needle-like, leading to the possible conclusion that the surface effect might have favored the selective growth of the 191 phase; however, this is doubtful, since the structures of the 191 and 194 phases are similar except for how they are stacked (Figure 1) and their surface energies are not likely to differ by much.

■ CONCLUSIONS

To investigate why WB_2-191 is more difficult to synthesize than MoB_2-191, we calculated the dependence of their lattice constants and total energies on the quantity of boron defects. We found that both 191 phases, which are unstable without B defects, are gradually stabilized as the number of defects increases (Figure 6). In our model, WB_{2-x}-191 and MoB_{2-x}-191 are the most stable at $x = 0.375$, which, along with their lattice constants (Figure 4), agrees closely with the experimental results for MoB_{2-x}-191. At this composition, the relative total energy of MoB_{2-x}-191 (−0.096 eV) is 1.63 times lower than that of WB_{2-x}-191 (−0.059 eV) which explains why MoB_{2-x}-191 is easier to synthesize. The mechanism of stabilization was revealed by the variation of their DOSs (Figure 7) where antibonding electrons decreased as B defects increased, reaching a minimum at $x = 0.375$.

Our calculations indicated that MoB_{2-x}-191 becomes stable at 0 K, but it is experimentally synthesized no lower than 1517 °C (1790 K). Considering this calculation error, it is not clear if WB_{2-x}-191 becomes stable since WB_{2-x}-191 is less stable than MoB_{2-x}-191. We made an attempt to synthesize WB_{2-x}-191 at its optimum composition, $x = 0.38$, at high temperature but found no traces of it. We have concluded that WB_{2-x}-191 cannot exist stably in the W−B binary system.

We reexamined the report on WB_2-191 by Woods et al.[1] based on our results. Although their lattice constants were close to those in our calculations, the synthesis temperature, 800 °C, was much lower than we expected from our calculations, and it was unlikely their sample happened to have the optimum amount of B defects. In the light of these facts, it appears probable that their sample included impurities that enabled its synthesis at low temperature.

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Notes

The authors declare no competing financial interest.

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