Anomalous lattice stiffening in tungsten tetraboride solid solutions with manganese under compression

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Abstract

Tungsten tetraboride (WB\textsubscript{4})-based solid solutions represent one of the most promising superhard metal candidates; however, their underlying hardening mechanisms have not yet been fully understood. Here, we explore the lattice compressibility of WB\textsubscript{4} binary solid solutions with different manganese (Mn) concentrations using high-pressure x-ray diffraction (XRD) up to 52 GPa. Under initial compression, the lattices of low and high Mn-doped WB\textsubscript{4} alloys (i.e. W\textsubscript{0.96}Mn\textsubscript{0.04}B\textsubscript{4} and W\textsubscript{0.84}Mn\textsubscript{0.16}B\textsubscript{4}) are shown to be more and less compressible than pure WB\textsubscript{4}, respectively. Then, a c-axis softening is found to occur above 39 GPa in WB\textsubscript{4}, consistent with previous results. However, an anomalous sudden a-axis stiffening is revealed at \textasciitilde36 GPa in W\textsubscript{0.96}Mn\textsubscript{0.04}B\textsubscript{4}, along with suppression of c-axis softening observed in WB\textsubscript{4}. Furthermore, upon Mn addition, a simultaneous stiffening of a- and c-axes is demonstrated in W\textsubscript{0.84}Mn\textsubscript{0.16}B\textsubscript{4} at \textasciitilde37 GPa. Speculation on the possible relationship between this anomalous stiffening and the combined effects of valence-electron concentration (VEC) and atomic size mismatch is also included to understand the origin of the nearly identical hardness enhancement in those two solid solutions compared to WB\textsubscript{4}. Our findings emphasize the importance of accurate bonding and structure manipulation via solute atoms to best optimize the hardness of WB\textsubscript{4} solid solutions.

Keywords: superhard, WB\textsubscript{4}, solid solution, lattice compressibility, high pressure, XRD

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1. Introduction

The development of superhard materials based on transition metal (TM) borides has recently attracted a great deal of attention due to potential applications in cutting and forming tools and wear-resistant coatings [1–3]. With a flexibility to simultaneously optimize covalent bonding and valence-electron density, TM borides exhibit not only a wide range of mechanical, thermal and electronic properties, but also a variety of crystal lattices with different connectivity of boron atoms ranging from isolated borons to boron networks to a boron skeleton [1–8]. Among these, the highest boride of tungsten, i.e. tungsten tetraboride (WB4), is of specific interest because of its extremely high Vickers hardness of ~43 GPa (0.49 N applied load), high bulk modulus of 326–339 GPa, high differential stress of up to ~19.7 GPa and lower cost constitutes as compared with other borides (e.g. ReB2, OsB2) [9–12]. Moreover, the hardness of WB4 can be dramatically enhanced via solid solution and extrinsic effects such as second phase and morphology change [13–17]. The maximum low-load bound estimate of compressive yield strength in WB4 solid solution and extrinsic effects such as second phase.

Moreover, the hardness of WB4 can be dramatically enhanced via solid solution and extrinsic effects such as second phase and morphology change [13–17]. The maximum low-load hardness values obtained for various WB4 alloys are summarized in supporting information table 1 (stacks.iop.org/JPhysCM/32/165702/mmedia). Particularly for the intrinsic solid solution hardening, TM dopants of varying valence electron count and atomic size can be incorporated into WB4 lattice owing to its unique defective cubic dodecaboride structure, which had caused several unusual hardening behaviors [17, 18]. For instance, all the optimized Vickers hardness values in WB4 binary solid solutions were achieved at rather low content of the dopants, e.g. 2.0 at. % for Ta, 4.0 at. % for Mn and 10.0 at. % for Cr. Besides, two nearly equivalent hardness values were observed in WB4 solid solutions with 4.0 and 10.0 at. % Mn, suggesting that multiple hardening mechanisms are at work. Further hardness increase was observed in ternary solid solutions (e.g. W0.94Ta0.02Mn0.04B4 and W0.97Ta0.02Cr0.05B4). Therefore, a full understanding of the underlying mechanisms for those hardness enhancements observed in WB4-based solid solutions is crucial to guide the design of new superhard borides.

Superhard materials generally possess a high bulk modulus, high shear modulus and a high shear strength [19]; thus, high-pressure studies were used to explore the lattice compressibility and lattice-supported differential stress (a lower-bound estimate of compressive yield strength) in WB4 solid solutions [10, 11, 17, 18, 20–23]. In pure WB4, by using high-pressure x-ray diffraction (XRD), Xie et al found a more compressible a-axis than the c-axis up to 42 GPa and then a discontinuous change in the slope of c/a ratio at ~42 GPa caused by sudden softening of c-axis [11]. They proposed it to be a reversible second-order phase transition owing to the rigid structure of WB4. Then, the same authors performed a comprehensive radial XRD study on WB4 and WB4 solid solutions under non-hydrostatic pressure [10, 18]. By comparing the lattice-supported differential stress, they attempted to distinguish between various hardening mechanisms such as electronic structure effect, atomic-size mismatch effect and extrinsic effects. However, except for the ternary solid solution W0.93Ta0.02Cr0.05B4 [17], the lattice compressibility of other WB4 binary solid solutions can hardly be found in the literature and thus remains unknown yet. Actually, several counterintuitive phenomena had already been demonstrated in W0.93Ta0.02Cr0.05B4 [17]. Specifically, this compound showed an abnormal small increase in bulk modulus based on the second-order fits as compared to WB4, which contrasts the Vegard’s law for solid solutions as neither Ta nor Cr borides are predicted to be stiffer than WB4. In addition, W0.93Ta0.02Cr0.05B4 was less compressible in the a-axis than it is along the c-axis and showed no signs of lattice instability, indicating a complete suppression of the pressure-induced phase transition observed in pure WB4. Those results raise several critical questions: (1) How can the TMs with different atomic size and valence electron count affect the anisotropy of lattice compression and the lattice instability in WB4-based binary solid solutions? (2) How would the lattice deformation behaviors evolve with TMs concentration?

In this work, we performed synchrotron-based XRD experiments using a diamond anvil cell (DAC) to evaluate the anisotropy of the lattice deformation behaviors and compressibility in WB4 solid solutions with low and high Mn concentrations. We specifically examined the TM element of Mn, because of the much smaller atomic radius of Mn (Mn = 1.32 Å) than tungsten (W = 1.41 Å; note B = 0.78 Å), the larger valence electron counts of Mn (Mn, Group VII) than tungsten (W, Group VI), and the unusual two hardness maxima observed in low and high Mn-doped WB4 [17]. A parallel set of experiments were also performed on pure WB4, which allows us to make a comparison of the lattice behaviors as objective as possible. We surprisingly find a successive stiffening of the a- and c-axes in low and high Mn-doped WB4 alloys, which contrasts prominently to pure WB4. Those findings point out to the significance of accurate manipulation of valence-electron concentration (VEC) and atomic size mismatch via solute atoms to best optimize the hardness of WB4-based solid solutions.

2. Experiments procedure

WB4 alloys with Mn were synthesized from the pure elements using hot pressing similar to our previously reported method [24]. Specifically, high-purity powders of tungsten (99.95% in purity), manganese (99.99% in purity) and amorphous boron (99.99%) at desired set of compositions (WB4, W0.96Mn0.04B4 and W0.84Mn0.16B4) were first ground together thoroughly in an agate mortar and pestle to obtain homogeneous mixtures. Then, the mixed powders were cold-pressed into cylindrical samples of 4 mm in diameter and 3 mm in height. Finally, the samples were carried out in a cubic anvil HPHT apparatus (SPD-6 × 600) at a temperature of 2300 K and a pressure of 5.2 GPa for a holding time of 15 min. The as-synthesized ingots were cut into halves for further analysis. One half was crushed into a fine sub-40 μm powder and used to confirm the phase purity by XRD. The XRD patterns were collected on a Bruker D8-Advanced x-ray diffractometer using Cu Kα radiation, with a scan range of 10° < 2θ < 100°. Because of the possible volatility of metal elements, inductively coupled plasma mass
spectrometry (ICP-MS) was used to confirm their concentration in the final samples. The other half samples were polished to an optically flat surface using polishing machine equipped with diamond films of 1600 mesh and emery papers of 800–2000 grit sizes. Then, the polished samples were used for surface characterization by scanning electron microscope (SEM) as well as Vickers hardness measurement using a micro-hardening tester equipped with a pyramid diamond indenter tip. For hardness test, the samples were indented using five different applied loads (i.e. 0.49, 0.98, 1.96, 2.94, 4.9, and 9.6 N) with a dwell time of 15 s.

In-situ high-pressure XRD experiments were carried out at the 4W2 beamline of the Beijing Synchrotron Radiation Facility (BSRF) by angle-dispersive measurements with a wavelength of 0.6199 Å and focused x-ray beam size of 26 × 8 μm² (FWHM). Pressure was generated by a symmetric piston-cylinder type DAC with a pair of diamond anvils having a cuvet size of 300 μm. A rhenium (Re) gasket pre-indented to 30 μm in thickness with a drilled hole of 110 μm in diameter was used into the chamber with silicone oil as the pressure-transmitting medium. The pressure was determined by ruby fluorescence method. The diffraction patterns of the sample were recorded using a 2D PILATUS detector and integrated using the FIT2D software [25]. Rietveld refinements on high-pressure data were carried out with the GSAS package [26].

3. Results

The phase purity of the as-synthesized WB₄, W₀.₉₆Mn₀.₀₄B₄ and W₀.₈₄Mn₀.₁₆B₄ samples was first examined using XRD. As shown in figure 1(a), the XRD patterns of the samples match very well with the reference data available for pure WB₄ in the JCPDS database [27]. In addition, they have no extra diffraction peaks corresponding to the impurity phases of WB₂ with increase of Mn concentration (figure 1(a)). Actually, the angle direction shift of the diffraction peaks towards higher 2θ indicates that the lattice of W₀.₉₆Mn₀.₀₄B₄ may be more compressible than that of WB₄, whereas W₀.₈₄Mn₀.₁₆B₄ can support a higher uncompressible lattice, indicating an anomalous modification of the WB₄ lattice compressibility by different Mn concentration.

Figure 2 shows the pressure-induced evolution of the XRD patterns for WB₄, W₀.₉₆Mn₀.₀₄B₄ and W₀.₈₄Mn₀.₁₆B₄. The pure WB₄ exhibits six diffraction peaks (101, 002, 110, 201, 112, 103), and no evidence of dramatic peak broadening or peak splitting was observed over the entire pressure range (figure 2(a)), which is consistent with previous results [11, 22]. All the Bragg peaks are also well preserved for the two solid solutions under compression, without unusual peak broadening or splitting. However, it is reasonable to conclude that, just like WB₄, the two solid solutions also remain in the hexagonal crystal structure up to the highest pressure of ~52 GPa. However, it is noteworthy that the two solid solutions exhibit obviously different pressure dependence as compared to WB₄. For example, with pressure increasing to ~52 GPa, the (110) peak in WB₄ shows a shift of Δθ = 0.5° toward high angle, as compared to Δθ = 0.7° and 0.3° in W₀.₉₆Mn₀.₀₄B₄ and W₀.₈₄Mn₀.₁₆B₄, respectively. Similar tendency is also illustrated by comparing the pressure evolution of other peaks. These preliminary XRD results have already indicated that the lattice of W₀.₉₆Mn₀.₀₄B₄ may be more compressible than that of WB₄, whereas W₀.₈₄Mn₀.₁₆B₄ can support a higher uncompressible lattice, indicating an anomalous modification of the WB₄ lattice compressibility by different Mn concentration.

Figure 3 shows the normalized unit cell volume as a function of pressure for the solid solution samples, with the best Riveted refinement patterns shown in supporting information figure 2. Because the reported zero-pressure bulk modulus of pure WB₄ was shown to depend critically on the pressure range and the choice of EOS [11, 17], we first investigate the compressibility of the fractional a- and c-lattice parameters (figure 4) to examine the structural stability in relation to Mn concentration. From figure 4, it can be observed that under initial compression, pure WB₄ is less compressible (i.e. stiffer) in the c-axis than it is along the a-axis, with both lattice constants showing a smooth decrease up to 39 GPa. However, further compression at ~39 GPa results in a sudden softening of the c-axis, which becomes significantly more compressible than the a-axis that does not show any change in behavior. These behaviors for WB₄ are in good agreement with previous results by Xie et al [11]. However, a number of other extraordinary trends are demonstrated for the Wₓ₋ₓMnₓB₄ solid solutions. In particular, just like WB₄, both W₀.₉₆Mn₀.₀₄B₄ and W₀.₈₄Mn₀.₁₆B₄...
show a linear decrease in the $a$- and $c$-lattice constants up to a pressure of ~36 GPa, with the $a$-axis being the most compressible one; nevertheless, $W_{0.96}Mn_{0.04}B_4$ is apparently more compressible than $WB_4$, as compared to the close compressibility between $W_{0.84}Mn_{0.16}B_4$ and $WB_4$. Besides, the linear compressibility between the $a$- and $c$-axes in $W_{0.96}Mn_{0.04}B_4$ ($\beta_{a\text{-axis}} = 1.32 \times 10^{-3} \text{ GPa}^{-1}$ and $\beta_{c\text{-axis}} = 1.14 \times 10^{-3} \text{ GPa}^{-1}$) and $W_{0.84}Mn_{0.16}B_4$ ($\beta_{a\text{-axis}} = 0.726 \times 10^{-3} \text{ GPa}^{-1}$ and $\beta_{c\text{-axis}} = 0.658 \times 10^{-3} \text{ GPa}^{-1}$) appears to be much more similar than that of pure $WB_4$ ($\beta_{a\text{-axis}} = 0.882 \times 10^{-3} \text{ GPa}^{-1}$ and $\beta_{c\text{-axis}} = 0.701 \times 10^{-3} \text{ GPa}^{-1}$), indicating the creation of a much more isotropic bonding after the addition of Mn in $WB_4$. This result agrees well with the general trend that isotropic structures favor high hardness [11]. Most interestingly, as the pressure increases above 36 GPa, the $c$-axis in $W_{0.96}Mn_{0.04}B_4$ continues to have a smooth decrease, whereas the $a$-axis appears to undergo a sudden stiffening and becomes obviously less compressible than the $c$-axis. Furthermore, with the increase of Mn concentration in $W_{0.84}Mn_{0.16}B_4$, not only the $a$- but also $c$-axes simultaneously exhibit a tendency for stiffening after 37 GPa and are characterized by comparable compressibility afterwards. Such a strengthening of the $a$- and $c$-axes observed in $WB_4$–Mn solutions are drastically distinct from the lattice softening in pure $WB_4$ as well as the swap of the most compressible direction from $a$- to $c$-axis in $W_{0.93}Ta_{0.02}Cr_{0.05}B_4$ alloy [10, 11, 17], suggesting that the addition of Mn can greatly modify the compressibility along different crystallographic axes in hexagonal $WB_4$.

The trends in bulk modulus change among the solid solution samples are then investigated (figure 3). Because of the extraordinary behaviors in the $a$- and $c$-directions and for a fair comparison with $WB_4$, fits to the Birch-Murnaghan EOS were performed at pressures before the occurrence of lattice stiffening in $WB_4$–Mn solid solutions (~36 GPa). For $WB_4$, we obtain $K_0 = 334 \pm 8 \text{ GPa}$ (second-order Birch–Murnaghan EOS) and $K_0' = 351 \pm 3 \text{ GPa}$ with $K_0' = 1.3 \pm 0.6$ (third-order Birch–Murnaghan EOS) (table 1). Those values are in well accordance with the obtained pairs ($K_0, K_0'$) = (326 ± 3.4) and (369 ± 9, 1.2 ± 0.5) by Xie et al [11]. For $W_{0.96}Mn_{0.04}B_4$, the measured $K_0$ is 318 ± 7 GPa (second-order Birch–Murnaghan EOS) and 339 ± 2 GPa with $K_0' = 1.5 \pm 0.4$, which is about 4% smaller than that of $WB_4$. By contrast, the bulk modulus of $W_{0.84}Mn_{0.16}B_4$ is $K_0 = 352 \pm 13 \text{ GPa}$ (second-order Birch–Murnaghan EOS) and $K_0' = 366 \pm 6 \text{ GPa}$ with $K_0' = 2.9 \pm 0.4$, which is approximately 5% larger than that of $WB_4$. Besides, we note that the measured bulk modulus of
W$_{0.84}$Mn$_{0.16}$B$_4$ is similar to the previously reported bulk modulus for the hardest WB$_4$ solid solution of W$_{0.93}$Ta$_{0.02}$Cr$_{0.05}$B$_4$, having $K_0 = 346 \pm 3$ GPa from the second-order fit and $K_0 = 366 \pm 14$ GPa with $K'_0 = 2.6 \pm 0.9$ from the third-order fit over the pressure range of 0–40 GPa [17]. All the obtained values are summarized in table 1. The nonlinear decrease of the bulk modulus in W$_{1-x}$Mn$_x$B$_4$ is somewhat surprising, since the bulk modulus usually follows Vegard’s law for solid solutions [28] and MnB$_4$ was reported to have a bulk modulus (250–280 GPa) [29, 30] much smaller than pure WB$_4$. These extraordinary behaviors in lattice compressibility suggest that different strengthening mechanisms should be at work at different Mn concentrations.

4. Discussion

Just as WB$_4$, the diffraction patterns of WB$_4$, W$_{0.96}$Mn$_{0.04}$B$_4$ and W$_{0.84}$Mn$_{0.16}$B$_4$ samples as a function of increasing pressure. The Re peaks is from the gasket due to incomplete filtering of the tails of x-ray beam. The red dashed line highlights the movement of the (110) peak in different samples.

Figure 2. Representative XRD patterns for WB$_4$, W$_{0.96}$Mn$_{0.04}$B$_4$ and W$_{0.84}$Mn$_{0.16}$B$_4$ samples as a function of increasing pressure. The Re peaks is from the gasket due to incomplete filtering of the tails of x-ray beam. The red dashed line highlights the movement of the (110) peak in different samples.

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Figure 3. Normalized unit cell volume of WB$_4$, W$_{0.96}$Mn$_{0.04}$B$_4$ and W$_{0.84}$Mn$_{0.16}$B$_4$ plotted as a function of pressure. Solid symbols represent this study, and open symbols denote previous studies. All the solid lines are the fits to the Birch–Murnaghan EOS.

Figure 4. (a) The normalized lattice parameters and (b) $c/a$ ratio plotted as a function of pressure for the W$_{0.96}$Mn$_{0.04}$B$_4$ and W$_{0.84}$Mn$_{0.16}$B$_4$ solid solutions as compared to pure WB$_4$. The dashed lines highlight the discontinuity of the lattice parameter evolution for pure WB$_4$ (black), W$_{0.96}$Mn$_{0.04}$B$_4$ (blue) and W$_{0.84}$Mn$_{0.16}$B$_4$ (red), which can be related to the reduction of particle size and enhancement of lattice strain [31]. Thus, the possibility of a first-order phase transition can
At a slightly lower pressure of ~36 GPa in W0.96Mn0.04B4, this dramatic decrease in the c/a ratio is also demonstrated. Figure 4(b) shows that the samples all show a linear increase in the c/a ratio up to ~36 GPa. Then, the c/a ratio demonstrates a sudden drop at ~39 GPa for WB4 that is caused completely by c-axis softening, consistent with the observation at ~42 GPa by Xie et al [10, 11]. Although a more dramatic increase in the c/a ratio is also demonstrated at a slightly lower pressure of ~36 GPa in W0.96Mn0.04B4, this transition, associated by the suppression of c-axis softening observed in pure WB4, is dictated by an abrupt a-axis stiffening. In addition, with the increase of Mn concentration to 16 at. % Mn (i.e. W0.84Mn0.16B4), no significant changes in the c/a ratio are observed over the entire pressure range up to 52 GPa, which h can be accounted for by the simultaneous stiffening of the a- and c-axes at ~36 GPa. Similarly, we note that the W0.93Ta0.02Cr0.05B4 alloy also did not exhibit any drastic change in the c/a ratio; while the c-axis softening observed in pure WB4 was suppressed, this process was accompanied by a smooth decrease for both a- and c-axes [17]. Thus, it is important to understand the origins of those anomalous lattice behaviors in WB4–Mn solid solutions and to determine its correlation to the unique bonding structure in WB4.

At ambient conditions, the WB4 crystal lattice has recently been resolved to consist of alternating hexagonal layers of W and B atoms with some W-deficient sites filled randomly by boron trimers, which can couple with the B layers to produce slightly distorted cuboctahedral boron cages [9]. For the c-axis softening in pure WB4, Xie et al excluded the probability of electronic topological transitions or Lifshitz transitions, and ascribed it to a reversible second-order phase transition that requires structural rearrangements and bond optimizing to accommodate high compression [11]. Besides, our latest high-pressure x-ray absorption spectroscopy study on WB4 revealed that this transition can be initiated by the W-B bond weakening due to W 5d electron depletion. For W0.93Ta0.02Cr0.05B4, Mohammadi et al also proposed that the suppression of c-axis softening observed in pure WB4 as well as the swap of the most compressible direction could stem from an electronic structure change with fundamentally altered bonding in the material [17]. Those results strongly suggest that in W0.96Mn0.04B4, the suppression of c-axis softening should also be dominated by electronic structure effect, i.e. maximized W–B or B–B bond covalency of the rigid cage-like boron structure along the c direction arising from optimized VEC. In the meanwhile, because Mn has a much smaller atomic radius than W, the additional a-axis stiffening in W0.96Mn0.04B4 should be attributed to atomic size effects that can influence available slip systems in a-b plane. However, as the Mn concentration increases, Xie et al [18] proposed that while the size mismatch effect should be improved, the optimal VEC might be exceeded, thus leading to a lower differential strain. Accordingly, the high hardness observed for the 10.0 at. % Mn sample (supporting information table 1) was attributed to dispersion hardening arising from the appearance of a second phase of MnB12. However, the results of Mohammadi et al showed that MnB12 starts to show up as an impurity phase only at and above 20 at. % Mn addition [17]. Also, we did not observe the presence of MnB12 in the sample of W0.84Mn0.16B4, thus excluding the possibility of an extrinsic effect. Moreover, our high-pressure result shows that when a higher concentration of Mn (16.0 at. %) is used, the c-axis actually becomes somewhat much stiffer than pure WB4, suggesting the preservation of optimized VEC. This behavior might be due to the fact that adding Mn can not only increase VEC but also induce changes either in W vacancies or in the spatial distribution of boron cages, which can in turn optimize the VEC. Due to the bulk modulus’ dependency on the spatially averaged VEC, the ~5% increase in the bulk modulus of W0.84Mn0.16B4 relative to the pristine WB4 (table 1) can be caused by the increased VEC. Moreover, the a-axis stiffening in W0.84Mn0.16B4 shows a much larger magnitude than that in W0.96Mn0.04B4, which is also compatible with the enhanced size mismatch effect. Therefore, these results suggest that the nearly identical hardness values in these

| Pressure (GPa) | WB4 | W0.96Mn0.04B4 | W0.84Mn0.16B4 |
|---------------|-----|---------------|---------------|
| 39 | 334 (8) | 4 | — | — |
| | 351 (3) | 1.3 (6) | — | — |
| 36 | — | — | 318 (7) | 4 |
| | — | — | 339 (2) | 1.5 (4) |
| 37 | — | — | — | — |

Table 1. Comparison of the experimental results for the bulk modulus $K_0$ (GPa) and their first derivative $K'_0$. Error values are quoted in parentheses.
two solid solutions of $W_{0.96}\text{Mn}_{0.04}B_4$ and $W_{0.84}\text{Mn}_{0.16}B_4$ can originate from the combined intrinsic effects of atomic size mismatch and electronic structure change, and the latter may manifest itself as a dynamic optimization of VEC with Mn concentrations that is associated with modification of tungsten vacancies and boron trimers distribution in the 3D boron network of WB$_4$.

5. Conclusions

In summary, we have employed high-pressure XRD to explore the lattice compressibility of WB$_4$–Mn solid solutions up to 52 GPa. We find that the low and high Mn-doped WB$_4$ alloys (i.e., $W_{0.96}\text{Mn}_{0.04}B_4$ and $W_{0.84}\text{Mn}_{0.16}B_4$) are respectively more and less compressible than pure WB$_4$ under initial compression. Then, a lattice softening is shown to occur in the $c$ direction above 39 GPa in pure WB$_4$, consistent with previous results. However, upon the addition of 4.0 at. % Mn to WB$_4$, it is surprising that an abrupt $a$-axis stiffening along with suppression of the $c$-axis softening observed in pure WB$_4$ is revealed at ~36 GPa. Moreover, when a higher concentration of Mn (16.0 at. %) is used, a simultaneous stiffening of the $a$- and $c$-axes is demonstrated at ~36 GPa. Without the presence of second phase, these results suggest that the nearly identical hardness values in these two solid solutions can originate from the combined intrinsic effects of atomic size mismatch and electronic structure change, which can manifest itself as a dynamic optimization of VEC with Mn concentration that is associated with a modification of tungsten vacancies and boron trimers distribution in the 3D boron network of WB$_4$. Our findings emphasize the importance of the best optimization and manipulation of the bonding and structure via solute atoms to the rational design of novel WB$_4$-based materials with enhanced mechanical properties.

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