Supporting Information:

Understanding Hardness of Doped $WB_{4.2}$

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Choice of DFT functional

For this work we have decided to use PBE[S1,S2] functional for all *ab initio* DFT computations. The functional is *de facto* standard for the majority of solid state calculations and became a power tool in investigating the $WB_{4.2}$ and its properties.[S3–S5] Even though PBE has been known to underestimate mechanical properties of materials,[S6,S7] it is sufficient enough for bonding analysis and is computationally easy to evaluate.

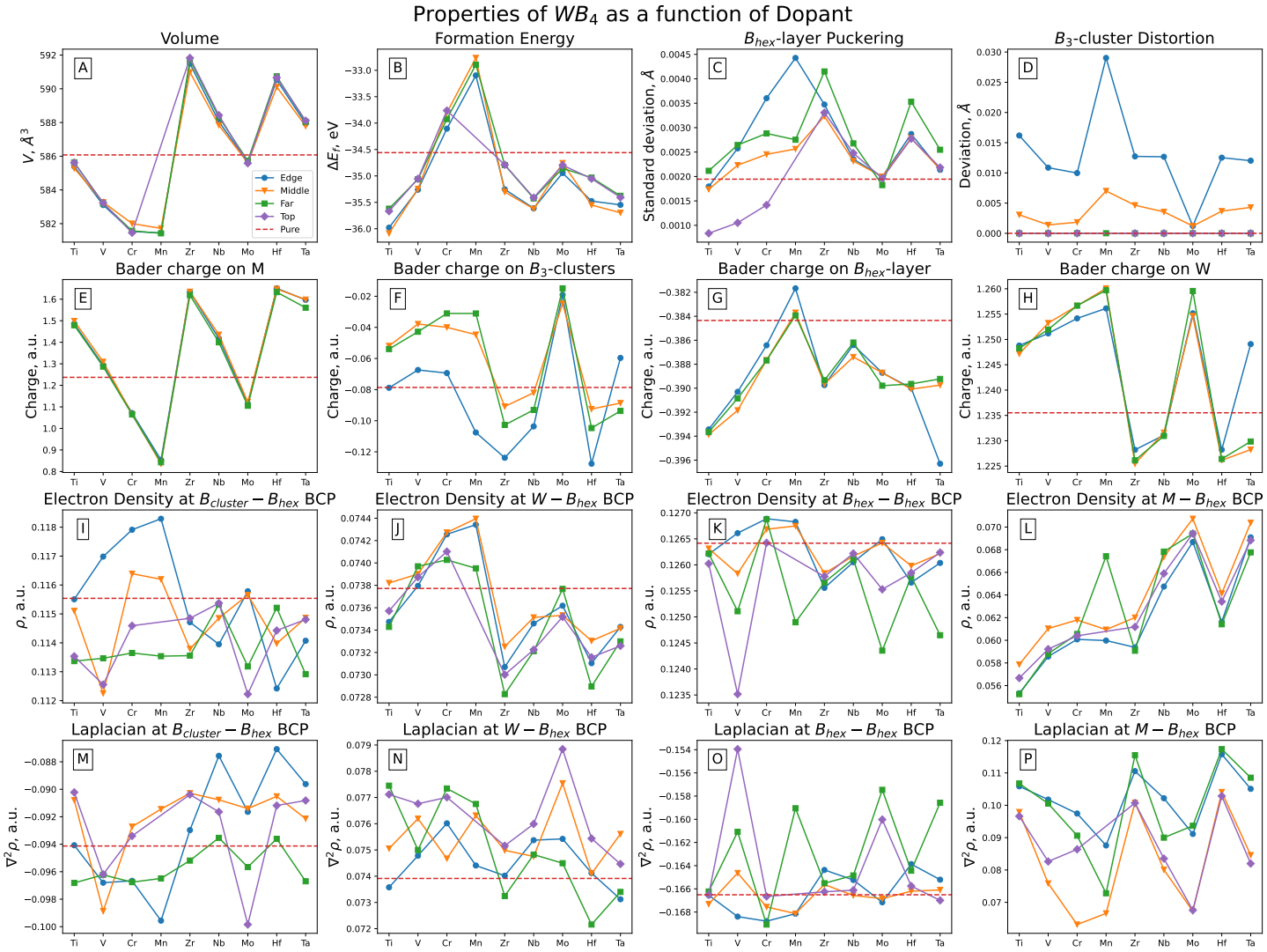

Figure S1: Geometric, thermodynamic, and QTAIM properties of selected bond of doped and pure structures. (A)—volume of the supercell. (B)–formation energy of the doped structure. (C)—average B_{hex} layer puckering, defined as standard deviation of c-fractional coordinate. (D)—B_3 distortion, defined as standard deviation of edges of the triangle, where average is taken to be the side of the equilateral triangle with the same area. (E)—Bader charge on M. (F)—total Bader charge on B_3. (G)—average Bader charge on B atom in B_{hex}—layer. (H)—average Bader charge on W. (I, M)—average ρ and $\nabla^2\rho$, respectively, at $B_{cluster}$−B_{hex} bond critical points. (J, N)—average ρ and $\nabla^2\rho$, respectively, at W−B_{hex} bond critical points. (K, O)—average ρ and $\nabla^2\rho$, respectively, at B_{hex}−B_{hex} bond critical points. (L, P)—average ρ and $\nabla^2\rho$, respectively, at M−B_{hex} bond critical points.

References

(S1) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

(S2) Perdew, J. P.; Burke, K.; Ernzerhof, M. Errata: Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1997**, *78*, 1396–1396.

(S3) Kvashnin, A. G.; Rybkovskiy, D. V.; Filonenko, V. P.; Bugakov, V. I.; Zibrov, I. P.; Brazhkin, V. V.; Oganov, A. R.; Osiptsov, A. A.; Zakirov, A. Y. WB_{5-x}: Synthesis, Properties, and Crystal Structure—New Insights into the Long-Debated Compound. *Adv. Sci.* **2020**, *7*, 2000775.

(S4) Dong, J.; Li, H.; Wang, J.; Guo, Z.; Liao, J.; Hao, X.; Zhang, X.; Chen, D. Nonrandomly Distributed Tungsten Vacancies and Interstitial Boron Trimers in Tungsten Tetraboride. *J. Phys. Chem. C* **2019**, *123*, 29314–29323.

(S5) Pan, Y.; Wang, X.; Li, S.; Li, Y.; Wen, M. DFT prediction of a novel molybdenum tetraboride superhard material. *RSC Adv.* **2018**, *8*, 18008–18015.

(S6) Råsander, M.; Moram, M. A. On the accuracy of commonly used density functional approximations in determining the elastic constants of insulators and semiconductors. *J. Chem. Phys.* **2015**, *143*, 144104.

(S7) Zhang, G. X.; Reilly, A. M.; Tkatchenko, A.; Scheffler, M. Performance of various density-functional approximations for cohesive properties of 64 bulk solids. *New J. Phys.* **2018**, *20*.