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First-principles calculation of structural, thermodynamic and mechanical properties of 5d transitional metal triborides TMB_3 ($TM = Hf–Au$)

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ABSTRACT

Due to their useful physical and chemical characteristics, transitional metal borides have attracted much attention. In this study, the structural, thermodynamical, mechanical, dynamical and electronic properties of 5d transitional metal triborides TMB_3 ($TM = Hf–Au$) are investigated by density functional theory. For each triboride, five structures are considered, i.e., m-AlB_2 (modified AlB_2), OsB_3, FeB_3, WB_3 and TcP_3 structures. The calculated lattice parameters are in good agreement with previously theoretical results. Thermodynamic stability of compounds is predicted and the formation enthalpy increases from TaB_3 to AuB_3. The calculated phonon dispersion curves demonstrate that each TMB_3 in the most stable structure is dynamically stable. The calculated density of states shows that they are all metallic. Among the studied compounds, OsB_3-ReB_3 (OsB_3-ReB_3 represents ReB_3 in OsB_3 structure, the same hereinafter) has the largest shear modulus (261 GPa), bulk modulus (355 GPa) and Young modulus (630 GPa). WB_3-WB_3 has the second largest shear modulus (257 GPa). This suggests that OsB_3-ReB_3 and WB_3-WB_3 might be potential ultra-incompressible and superhard materials.

1. Introduction

Since 2004 [1,2], a wide variety of transitional metal borides have been synthesized at ambient condition, high pressure or high temperature. Transitional metal borides, which include OsB_2, ReB_2, CrB_4 and WB_4 were reported with unique physical and chemical characteristics [1–5], such as high shear modulus (more than 200 GPa) and Young modulus (more than 550 GPa). Therefore, transitional metal borides have attracted much attention [1–6]. In 2007, rhenium diboride (ReB_2) has been synthesized by Chung et al. in bulk quantities via arc-melting under ambient pressure [5]. ReB_2 was reported to be an interesting candidate as an superhard material (Vickers hardness of 48 GPa under an load of 0.49 N), while scratch marks left on a diamond surface confirmed its superhard nature [5]. The compact crystal structure and the internal mechanisms of its hardness might be understood from the highly directional covalent bonds and the optimal filling of the bonding states [7–9]. In 2008, tungsten tetraborides (WB_4) has been synthesized by using arc-melting, and the hardness was measured to be 46.2 GPa under an applied load of 0.49 N [2]. Similar to ReB_2, the high hardness of WB_4 has been suggested to be related to the covalently bonded 3D framework [4]. Thus, WB_4 is thought to be an interesting candidate as a less expensive member of the growing group of superhard transitional metal borides [10]. However, our previous study indicated that WB_4 is thermodynamically unstable at ambient conditions with the formation enthalpy of 1.85 eV [11]. Moreover, the stoichiometry of WB_4 was recently challenged and suggested to be tungsten triborides (WB_3) [12], and the calculated results indicated that the nominal composition of WB_4 is defective tungsten borides ($W_{1-x}B_3$ ($x < 0.25$) or WB_{4-x} ($x > 0.25$)) through nonstoichiometric calculations and x-ray diffraction spectra [13]. Recently, Zhang et al. [14] have carried out first-principles calculations to evaluate the thermodynamic, mechanical, and phonon stabilities of WB_4 and WB_3, and the results indicated that only WB_3 was dynamically stable. The relaxed structure of WB_3 has been regarded as the absence of four boron atoms at 4f sites from the WB_4 structure. These results demonstrated that the tungsten boride prepared by Gu.et al. [2] and Mohammadi et al. [10] should

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be WB_3. Furthermore, a highly stable WB_3 with hR24 symmetry [15] have been identified by first-principles calculations, and it was found that such a noncompact and metallic system has an unexpectedly high hardness. In addition, other 5d transitional metal triborides like the OsB_3 (P-6m2) has been predicted by using the ab initio evolutionary structure prediction, and its predicted hardness was 36.9 GPa, which can considered as potential hard material [16]. Hence, it is interesting to systematically investigate the structure and mechanical properties of transitional metal triborides.

In the present study, the physical properties of 5d transitional metal triborides from HfB_3 to AuB_3 are systematically investigated by first-principles. For each boride, five structures are considered, i.e., m-AlB_2 (modified AlB_2), OsB_3, FeB_3, WB_3 and TcP_3 structures. The general trends are discussed and we hope that the obtained results might be important for designing new superhard materials.

2. Computational method and crystal structure

2.1. Computational method

All the calculations are performed within the CASTEP code [17], based on the density-functional theory (DFT). The code is suitable for calculations using periodic boundary conditions to infinite lattice system. The Vanderbilt US-PP [18], which describes the interaction of valence electrons with ions, is used with the same cutoff energy of 400 eV. The exchange and correlation functional are treated by the local density approximation (LDA) [19]. The k-points of 11 × 11 × 15 for m-AlB_2 (P6/mmm, No. 191), 12 × 12 × 7 for OsB_3 (P-6m2, No. 187), 11 × 11 × 5 for WB_3 ($P6_3/mmc$, No. 194), 11 × 15 × 8 for FeB_3 ($P2_1/m$, No. 11) and 12 × 16 × 8 for TcP_3 (Pnma, No. 62) structures are generated using the Monkhorst–Pack scheme [20,21]. Lattice parameters and atomic positions are optimized by Broyden–Fletcher–Goldfarb–Shanno (BFGS) method [22]. For the self-consistent field iterations, the convergence tolerances for geometry optimization are selected as the difference in total energy, the maximum ionic Hellmann–Feynman force, and the maximum displacement being within 1.0×10^{-6} eV/atom, 0.01 eV/Å, and 1.0×10^{-4} Å, respectively. The formation enthalpy is calculated by the following formula:

$$\Delta H^{TMB_3} = E^{TMB_3}_{total} - \left[E^{TM}_{solid} + 3E^{B}_{solid}\right]$$

where E for elemental boron is calculated based on the structure of alpha rhombohedral boron [23]. If the ΔH^{TMB3} is negative, the considered compound is thermodynamically stable. Otherwise, it is unstable. The calculated bulk modulus B and shear modulus G are from the Voigt-Reuss-Hill approximations [24–26]. Young's modulus E and Poisson's ratio ν are obtained by the following formula:

$$E = 9BG/(3B + G)$$

$$\upsilon = (3B - 2G)/[2(3B + G)]$$

2.2. Crystal structure

The considered crystal structures are plotted in Fig. 1. The m-AlB_2 structure can be derived from the AlB_2 structure by replacing one-third of the aluminum atoms with vacancy so that the remaining aluminum atoms form layers of open hexagons with alternate layers displaced by one atom [12]. In m-AlB_2 structure (Fig. 1a), all the B atoms are sevenfold coordinated with four TM (transitional metal) atoms and three B atoms. Each TM atom is located at the center of the hexagonal prism formed by twelve B atoms. OsB_3 structure (Fig. 1b) contains two formula units with the TM at site 2a (0, 0, 0), while the B atoms have two Wyckoff sites, i.e., 2b (0, 0, 1/2) and 2i (2/3, 1/3, 0.3253) [16]. Half of the B atoms are sevenfold coordinated with four B and three TM atoms, while the other half of the B atoms are located at the center of a trigonal bipyramid formed by six TM atoms and coordinated by two B atoms. Each TM atom is coordinated by eight B atoms and locates at

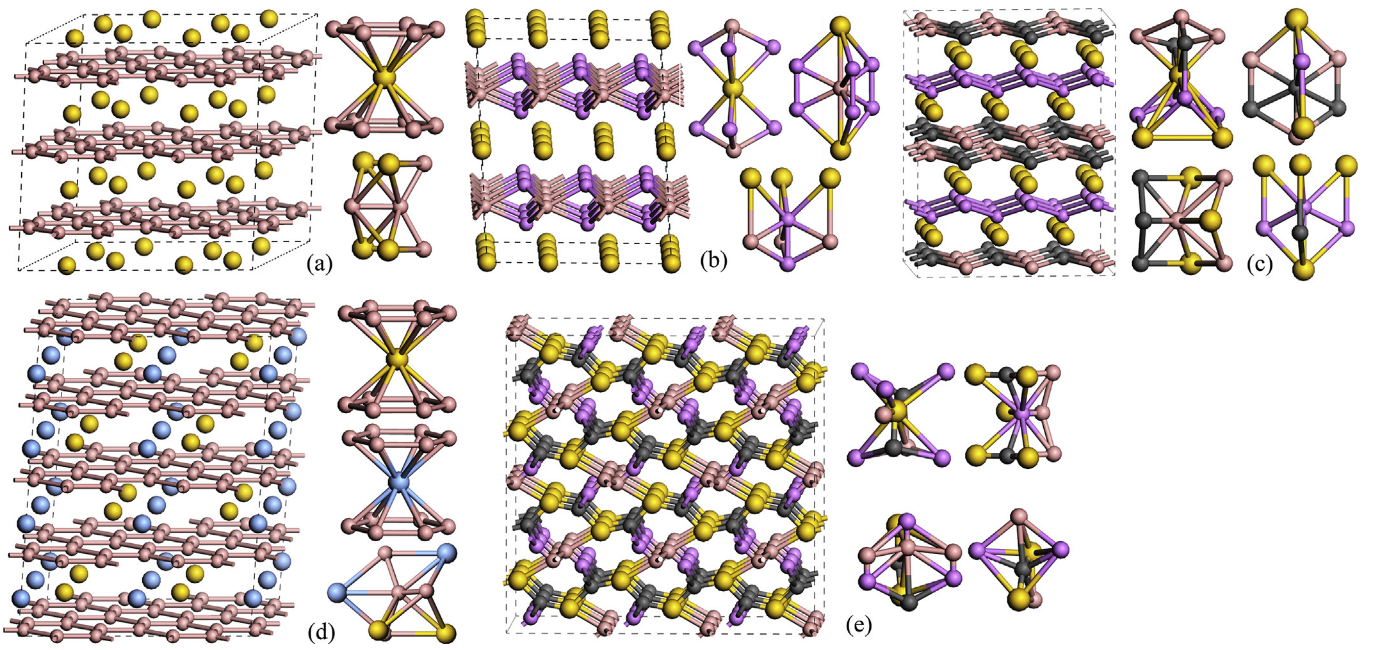

Fig. 1. Crystal structures and the nearest coordination numbers of TM and B in TMB_3: (a) m-AlB_2 structure, (b) OsB_3 structure, (c) FeB_3 structure, (d) WB_3 structure and (e) TcP_3 structure. The large and small spheres represent TM and B atoms, respectively. Different color spheres represent different Wyckoff sites, for instance, for each TM atom coordinated by the twelve B atoms in WB_3 type (d), but TM has two Wyckoff sites with different TM–B bond distances.