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Prediction on technetium triboride from first-principles calculations

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ABSTRACT

Taking the Tc-B binary system as an example, here we report the first-principles prediction on new phases of technetium borides, TcB_3, which has an unprecedented stoichiometry. Crystal structures, phase stability, electronic properties and mechanical properties of TcB_3 have been investigated using first-principles calculations. The hexagonal $P\bar{6}m2$ structure (No.187) TcB_3 with a high value of hardness (29 GPa) is energetically stable against decomposition into other compounds under pressures above 4 GPa, indicating that TcB_3 can be synthesized above this pressure.

1. Introduction

Transition metal borides have attracted continuing interests due to their outstanding physical properties and wide engineering applications [1–15]. Currently, great interest for transition metal borides has emerged based on the design concept for intrinsically superhard compounds that the interaction of boron atoms into the transition metal lattices to form strong covalent bonds. The Tc-B system is a typical binary system which has many different stoichiometries. Tc_7B_3, TcB_2 and Tc_3B have been synthesized and investigated for many years [16]. Extensive experimental and theoretical investigations have been carried out for technetium borides by changing the stoichiometry [5,16–20].

Zhang et al. [21] predicted a hexagonal $P\bar{3}m1$ structure for TcB, which is energetically more favorable than the previously reported $P\bar{6}m2$ [17] and *Cmcm* structures [22]. Aydin and Simsek [18] investigated the structure, mechanical and electronic properties of TcB_2 and also showed that TcB_2 in ReB_2-type is more energetically favorable than that of the AlB_2-type and it is a hard material. Deligoz et al. [23] investigated the lattice dynamical and thermodynamical properties for TcB_2 in the OsB_2-type structure. Wang et al. [5] in their first-principles calculations, suggested that TcB_4 in WB_4 structure might be superhard materials, and Zhang et al. [24] proposed that the predicted TcB_4 with MoB_4-type structure has lower formation enthalpy than TcB_4 with both the WB_4-type [5] and MnB_4-type [25].

Transition metal compounds usually have various stoichiometries and crystal structures due to the coexistence of metallic, covalent, and ionic bonds in them, and this flexibility provides a lot of candidates for materials design [26]. Recently, WB_3, ReB_3, OsB_3, IrB_3, MoB_3, RuB_3, CrB_3, and MnB_3 have been widely investigated experimentally and theoretically [24,27–38]. Because of technetium lies to the specific position in the periodic table, however, technetium triboride TcB_3 so far has never been synthesized nor theoretically studied. In this work, we systematically investigate the crystal structure, phase stability, electronic structure, and mechanical properties of TcB_3. Because chemically related compounds may have a similar structure, eight possible TcB_3 structures based on the theoretical and experimental structures of known transition-metal compounds were investigated using first-principles calculations, including ReB_3-type (hexagonal, $P\bar{3}m1$, No.164) [30], TcP_3-type (orthorhombic, *Pnma*, No.62) [32], OsB_3-type (monoclinic, $P2_1/m$, No.11) [27], MoB_3-type (hexagonal, $R\bar{3}m$, No.166) [24], ReB_3-type (hexagonal, $P\bar{6}m2$, No.187) [29,30], WB_3-type (hexagonal, $P6_3/mmc$, No.194) [31], ReB_3-type (hexagonal, $P6_3/mmc$, No.194) [30], and MnB_3-type (monoclinic, $C2/m$, No.12) [28]. The results show that the hexagonal $P\bar{6}m2$ structure (No.187) TcB_3 is stable mechanically, dynamically, and thermodynamically, and can be synthesized at high pressures.

2. Computational methods

In this work, the density functional theory (DFT) calculations were performed using the projector-augmented wave (PAW) method [39–41], as implemented in the Vienna Ab-initio Simulation Package (VASP) code [42]. The generalized gradient approximation (GGA) [43] with the Perdew-Burke-Ernzerhof (PBE) scheme was used to describe the exchange-correlation function. Geometry optimization was carried out using the conjugate gradient algorithm. The plane-wave cutoff energy was 500 eV. The k-points were generated using the

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Monkhorst-Pack mesh [44]. In order to obtain equilibrium lattice parameters for the various TcB_3 phases, the total-energy calculations were performed by changing the volume of the phases together with the ionic positions and the cell shape allowed to vary. These total energies were then fitted with the Birch-Murnaghan equation of state [45–47]. The elastic constants were calculated using the universal-linear-independent coupling-strains (ULICS) method [48], which is computationally efficient and has been widely used in calculations of single-crystal elastic constants [49–53]. Based on the single-crystal elastic constants, the bulk modulus B and the shear modulus G were calculated according to the Voigt-Reuss-Hill approximation [54]. Young's modulus E and Poisson's ratio ν were obtained by the following equation:

$$E = 9BG/(3B + G) \quad (1)$$

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

The estimated Vickers hardness (H_V) of these borides are relative to G and B through the empirical formula based on the Pugh modulus ratio k=G/B [55,56]:

$$H_V = 2(k^2G)^{0.585} - 3 \quad (3)$$

Phonon dispersion was calculated using density functional perturbation theory, as implemented in the PHONOPY code [57,58].

3. Results and discussion

As mentioned above, the predicted eight structures for TcB_3 are shown in Fig. 1. For comparison, the known technetium borides in the Tc-B phase diagram, i.e. TcB_2 (hexagonal, No.194), Tc_3B (orthorhombic, No.63) and Tc_7B_3 (hexagonal, No.186) are also included in the calculations. The formation enthalpy of the compound of Tc_xB_y was calculated using the following equation:

$$\Delta H = [H_{total}(Tc_xB_y) - (xH_{total}(Tc) + yH_{total}(B))]/(x + y) \quad (4)$$

where H, defined by $H = E + PV$, is the enthalpy of the corresponding

Table 1
Optimized lattice parameters a, b, and c (Å), cell volume (V in Å^3 per formula unit), and calculated formation enthalpy (ΔH in eV per atom).

Structure	a	b	c	V	ΔH
TcB_3-164(ReB_3)	2.861		4.646	32.94	−0.02
TcB_3-11(OsB_3)	4.114	2.883	5.856	34.24	−0.23
TcB_3-62(TcP_3)	11.185	2.854	4.552	36.33	−0.01
TcB_3-166(MoB_3)	5.193		9.333	36.33	−0.16
TcB_3-187(ReB_3)	2.908		4.572	33.48	−0.32
$TcB_3$194(WB_3)	5.256		5.980	35.76	−0.10
TcB3-12(MnB_3)	7.612	2.929	6.166	34.38	−0.27
TcB_3-194(ReB_3)	2.890		9.271	33.54	−0.28
TcB_2	2.897		7.461	27.12	−0.44
TcB_2[a]	2.892		7.453		
TcB_2[b]	2.877		7.421		
Tc_3B	2.911	9.236	7.212	48.48	−0.26
Tc_3B[a]	2.891	9.161	7.246		
Tc_3B[c]	2.919	9.283	7.265		
Tc_7B_3	7.482		4.851	117.58	−0.31
Tc_7B_3[a]	7.417		4.777		

[a] Ref.[16], Experiment.
[b] Ref.[18], VASP.
[c] Ref.[22], VASP.

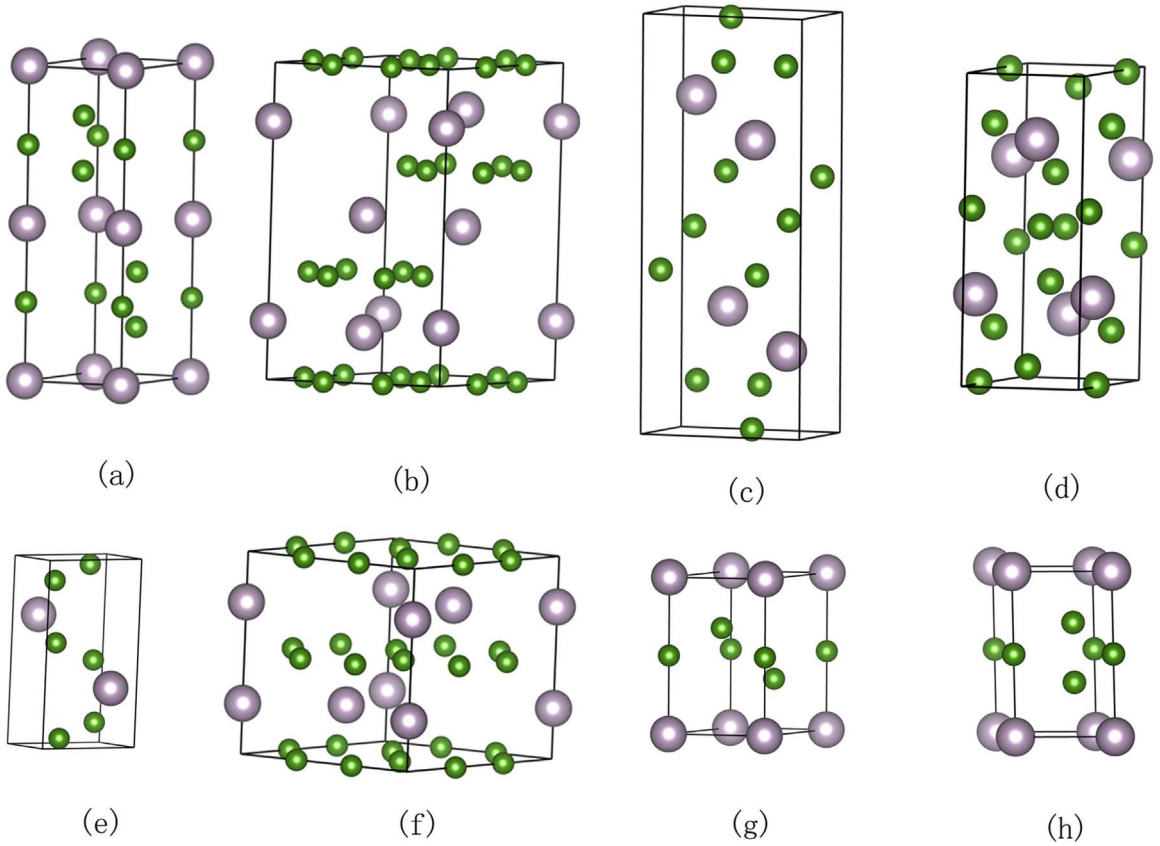

Fig. 1. Structure models of TcB_3: (a) ReB_3-type (hexagonal, No.194) : Tc 2a (0, 0, 0), B1 4f (0.3333, 0.6666, 0.6622), B2 2b (0, 0, 0.25); (b) MoB_3-type (hexagonal, No.166): Tc 6c (0, 0, 0.1849), B 18f (0.6714, 0, 0); (c) TcP_3-type (orthorhombic, No.62), Tc 4c (0.2040, 0.25, 0.1469), B1 4c (0.0159, 0.25, 0.3620), B2 4c (0.3822, 0.25, 0.3374), B3 4c (0.3877, 0.25, 0.9438); (d) MnB_3-type (monoclinic, No.12), Tc 4i (0.2878, 0, 0.7954), B1 4i (0.0067, 0, 0.7061), B2 4i (0.1741, 0, 0.4747), B3 4i (0.4348, 0, 0.1218), β=89.8518°; (e) OsB_3-type (monoclinic, No.11): Tc 2e (0.9157, 0.25, 0.6863), B1 2b (0.1911, 0.25, 0.0480), B2 2b (0.3911, 0.25, 0.5503), B3 2b (0.4889, 0.25, 0.8786), β=99.6875°; (f) WB_3-type (hexagonal, No.194): Tc1 2c (0.3333, 0.6666, 0.25), Tc2 2b (0, 0, 0.25), B 12i (0.6649, 0, 0); (g) ReB_3-type (hexagonal, No.164): Tc 1a (0, 0, 0), B1 2d (0.6666, 0.3333, 0.3334), B2 1b (0, 0, 0.5); (h) ReB_3-type (hexagonal, No.187): Tc 1a (0, 0, 0), B1 1b (0, 0, 0.5), B2 2i (0.6666, 0.3333, 0.3190). The large and small spheres represent Tc and B, respectively.