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Stability, chemical bonding behavior, elastic properties and lattice thermal conductivity of molybdenum and tungsten borides under hydrostatic pressure

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Abstract

The thermodynamic stability and mechanical properties of Mo–B and W–B binary compounds are investigated by first principles calculations and compared with other theoretical and experimental results. In order to determine the stability, compressive behavior and mechanical properties of Mo_2B_5 and W_2B_5 phases, hydrostatic pressure up to 10 GPa is applied to the crystal. The formation enthalpy, phonon spectrum, electronic structure and mechanical modulus at different pressure are obtained and variety of chemical bonding behavior has close relationship with the change of elastic properties. Temperature-dependent thermodynamics parameters of Mo_2B_5 and W_2B_5 are analyzed under different pressure. Moreover, the whole profile of temperature dependent lattice thermal conductivity of Mo_2B_5 and W_2B_5 from Debye temperature up to high temperature limit at different pressure is predicted by combining the Slack's, Clarke's and Cahill's model. The difference between the variation of lattice thermal conductivity of Mo_2B_5 along [001] and [100] directions is attributed to the anisotropic chemical bonding behavior of B–B bonds and M–B bonds under pressure effect.

Keywords: C. Mechanical properties; D. Borides; Stability; Lattice thermal conductivity; Pressure effect

1. Introduction

Boron is a common light element and can be combined with most metallic elements to form a variety of metal-rich and boron-rich borides [1]. The main driving force of the research effort on metal borides lies in their specific properties, for example, their mechanical behaviors, some of them being superhard compounds or considered as the potential ultrahard materials [2,3]. Also, superconductivity [4], thermoelectric [5] and specific magnetic behaviors are in the focus of metal boride research. More importantly, the compounds of transition metals (TM) with light elements B have been regarded as one of the recently developed groups of potential superhard materials because the interaction of these light-elements into the TM to form strong covalent bonds yet keeping a high valence-electron density (VED) and bulk moduli. Upon an increase in the boron to metal ratio, the B sublattice evolves from isolated clusters to extended one-, two-, and then three-dimensional boron frameworks [6,7]. OsB_2 was synthesized, followed by the hardest metal-based ReB_2 [8,9]. However, their prospective applications were questioned from the aspects of the functionality and cost of raw materials. So the highest borides of tungsten, molybdenum and chromium have recently stimulated much interest and become the prime candidate to be superhard materials. In recent years, the thermodynamic stability, electronic structure and mechanical properties of the mentioned borides are comprehensively studied in theoretical and experimental way [10–20]. For example, CrB_4 have been proved to be the potential superhard materials [21]. For the W–B system, more than 22 different structures have been found and systematically investigated [15,17], while the reported Mo–B binary phases are more than 20 species [10,12]. Among the W–B system, the main phase of W_2B_5

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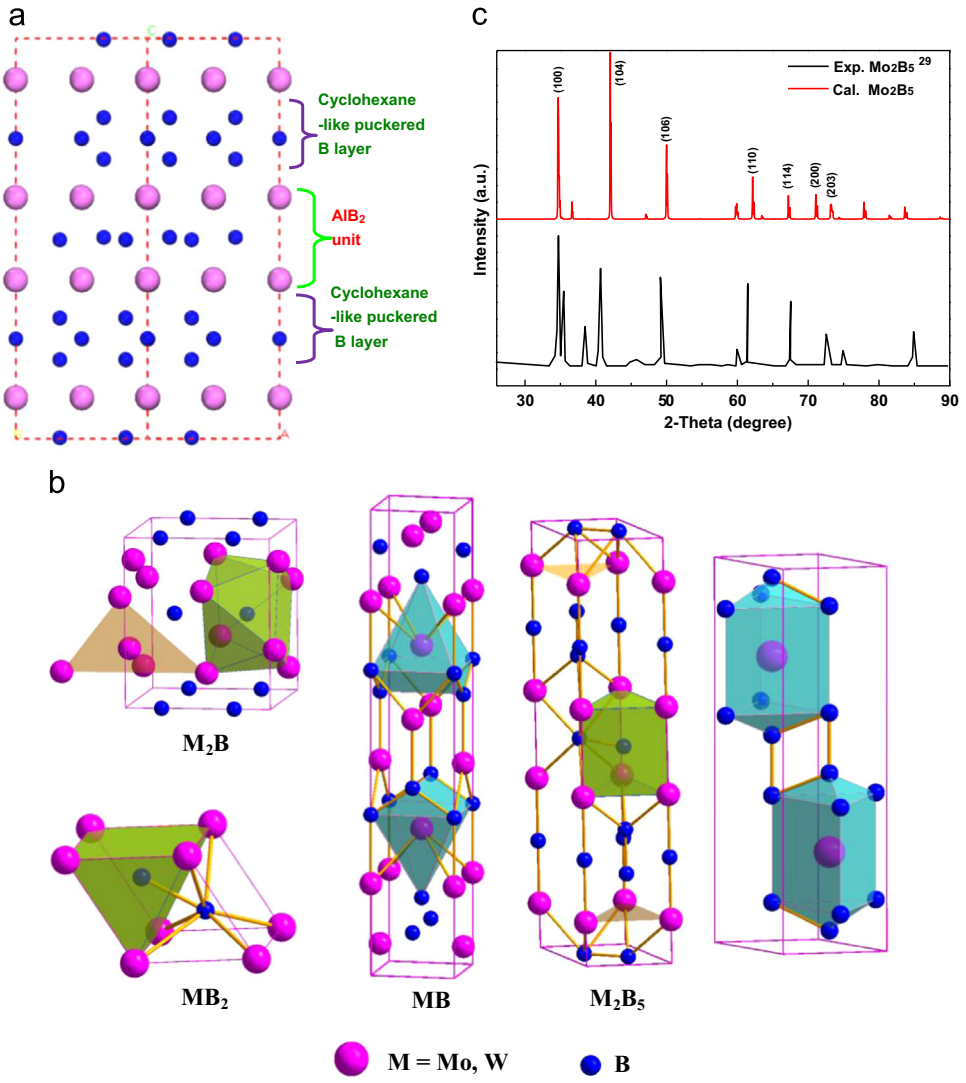

Fig. 1. (a) The $2 \times 2 \times 1$ supercell of M_2B_5 ($P6_3/mmc$, no. 194); (b) the crystal structures of Mo–B and W–B systems. The large pink ball represents the molybdenum or tungsten atoms and the small blue ball represents the boron atom. (c) The simulated XRD pattern together with the experimental data for Mo_2B_5 from Ref. [29]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

is illustrated in Fig. 1(a), in which the AlB_2 units are periodically stacked along the c axis with cyclohexane-like puckered B layers [22]. W_2B_5 was first synthesized with an assumed composition of $WB_{2.5}$ in hexagonal structure ($P6_3/mmc$, no. 194), but the positions of the B atoms could not be determined from the experiment and were tentatively assigned from the space considerations with a B composition of less than 68% [23]. Later, experimental spectroscopic data and the calculated densities of states of W_2B_5 illustrated that the theoretical shape of the occupied band was in agreement with the observed emission spectra, but the band position relative to the Fermi level was not, which might be related to the experimentally undetermined positions of B atoms [24]. Moreover, previous theoretical investigation revealed the instability of W_2B_5 [25]. So the literature references confirmed that one boron atom is absent, and the stoichiometric composition is actually WB_2 with a space group of $P6_3/mmc$ (no.194). In the same way, the Mo_2B_5 is confirmed to be MoB_2 phase (R3m, no.166). However, the previous investigation about the stability of W_2B_5 and Mo_2B_5 are all by experimental observation such as spectroscopic, X-ray and neutron powder diffraction. The elastic and dynamics stability and relationship between electronic structure and properties are rarely reported. First principle calculations become of utmost importance in order to shed light on the structure-property relationship in metal borides. In this paper, we firstly calculate the formation energy and mechanical properties of Mo–B and W–B binary system including M_2B (I4/mcm), MB (I41/amd, δ phase), MB_2 (P6/mmm, γ phase), M_2B_5 ($P6_3/mmc$, ε phase) and MB_4 ($P6_3/mmc$) (Fig. 1(b)) and then, in order to determine the stability, compressive behavior and mechanical properties of the Mo_2B_5 and W_2B_5, we performed a compression study on them up to 10 GPa.

The contribution of the present work is as follows: first, it is to provide a further and complementary understanding on the thermodynamic, elastic and dynamics stability of W_2B_5 and Mo_2B_5 phases under pressure effect. Second, it is to give a