

Theoretical study of structural, mechanical, thermal and electronic properties of Ti_3B_4 with Ta_3B_4 structure under high pressure



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ABSTRACT

We present a systematic theoretical study on the structural, electronic, elastic, and thermal properties of Ti_3B_4 in Ta_3B_4 structure under pressure. Our calculations indicate that the volume of Ti_3B_4 cell decreases about 12% of primary structure and the b axis length is shorten by 5% when the applied pressure is 36 GPa. The peak heights of DOS and PDOS curves of Ti_3B_4 are lower slightly when under high pressure. The calculated elastic constants and elastic modulus are all found to increase linearly by increasing pressure; and the heat capacity at constant volume (C_V) as a function of pressure are evaluated, which is more sensitive to the temperature than to the pressure. Meanwhile, the elastic anisotropy, phonon dispersion and corresponding phonon density of states with pressure are also calculated and discussed. The average LTEC of Ti_3B_4 is evaluated to be $8.6 \times 10^{-6} K^{-1}$ at room temperature, which may provide valuable datum for its thermal property investigation.

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1. Introduction

Titanium borides present quite attractive advantages such as the high melting point, hardness, wear resistance, thermal shock resistance, and electrical conductivity [1]. These characteristics make them widely used in industrial areas such as cutting tools, crucibles, electrode materials and wear-resistant parts [2,3].

In Ti–B binary system, Murray et al. [4] treated the solution phases TiB (Pnma) and TiB_2 (P6/mmm) as the stoichiometric compounds. By different methods, the existence of stoichiometric compound Ti_3B_4 was also confirmed by many researchers [5–7]. This compound has an orthorhombic Ta_3B_4 -type structure (Immm), and can form by a peritectic reaction between TiB_2 and metal liquid at very high temperature. However, the available literature data about peritectic reaction temperature is contradictory. In the publication [7] this reaction was assigned as 2333 K; while in the assessment [8] the reaction was assigned as 2477 K. To verify the temperature of this reaction, Witusiewicz et al. [9] performed some key experiments by XRD and DTA, based on which they put forward the peritectic reaction temperature of 2412 K.

The study of Ti–B binary system has been performed by many researchers [4–9], and much useful information has been achieved. However, up to now, some of their properties under pressure are still almost unknown. To our knowledge, there are only few published results about TiB_2 with AlB_2 structure under high pressure [10], and the published data for Ti_3B_4 ceramic under high pressure even do not exist. However, the study of the pressure behavior of hard materials is necessary. In our earlier work [11], the hardness of Ti_3B_4 was estimated to be as high as 33.1 GPa, which is just a little smaller than experimental datum of TiB_2 (35 GPa) [12]. Therefore, in present work, we will investigate the structural, electronic, mechanical, and lattice dynamical properties of Ti_3B_4 in Ta_3B_4 structure under high pressure.

2. Model and computational method

The crystal structure of Ti_3B_4 considered in this paper is shown in Fig. 1a, which consists of two alternative layers (layers A and B) in [010] direction. In large-scale image (2×2 in Fig. 1b), it can be clearly seen that both layers have the same atomic configuration, and layer B is a translation structure transformed from layer A by [0.500.5] fractional coordinate. Meanwhile, as illustrated in Fig. 1a, Ti_3B_4 could also be regarded as an intergrown structure consisting of two kinds of layered sub-structures. The middle sub-structure is similar to TiB_2 structure and the upper/lower

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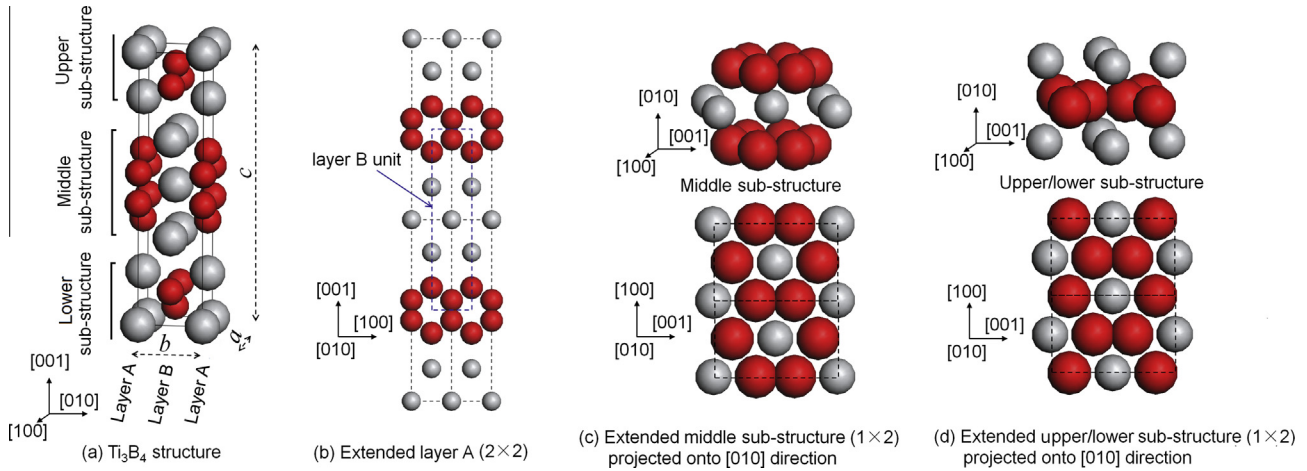


Fig. 1. Schematic diagrams of the structures for the titanium boride cell: (a) Ti_3B_4 structure, (b) extended layer A (2×2), (c) extended middle sub-structure (1×2) projected onto [010] direction, and (d) extended upper/lower sub-structure (1×2) projected onto [010] direction.

sub-structure belongs to layered Ti–B sub-structure. We show the extended middle, upper/lower sub-structures and their projection on [010] direction in Fig. 1c and d, respectively. Both of the sub-structures adopt a layered hexagonal structure with alternating close-packed layers of graphite-like boron and titanium layers.

The present work was carried out by using first-principles method based on the density functional theory (DFT), as implemented CASTEP code [13,14]. The ultrasoft pseudo-potentials (USPPs) were used to represent the interactions between ionic core and valence electrons. The valence electrons of Ti and B are considered as $3s^2 3p^6 3d^4 4s^2$, $2s^2 2p^1$, respectively. A plane-wave basis set with cut-off energy of 350 eV was used. For the exchange and correlation terms in the electron–electron interaction, Generalized gradient approximation (GGA) exchange–correlation energy of PBE approach was used for calculations [15]. For k -space summation the $8 \times 8 \times 2$ for Ti_3B_4 with Monkhorst–Pack scheme in the first irreducible Brillouin zone [16] was used. The elastic constants were calculated by means of linear fitting of the stress–strain curves based on the Hooker’s law [17]. The finite displacement method is applied to a supercell consisting of the geometrically optimized primitive lattice for calculating the phonon dispersion curves. The real space cutoff radius was set to 5 Å, which resulted in a supercell ($\text{Ti}_{24}\text{B}_{32}$) volume four times larger than the original unit cell. For thermal properties, the calculation method in details can be found in our past work [11]. In general, the commonly DFT gives the ground state total energy (E_{gs}) without considering the temperature effect. Then, the vibration free energy (F_{vib}) is calculated by phonon density of states at given volume using CASTEP code. We should note that for metallic Ti_3B_4 boride, the contribution of thermal electron must be considered for total Helmholtz free energy ($F(V, T)$). Finally, using data $F(V, T) - V$, the EOS at temperature T can be fitted; and the equilibrium volume $V(T)$ at T is obtained. The volumetric thermal expansion coefficient β can be calculated through $V(T) = (1 + \beta T)V_0$, where V_0 represents the equilibrium volume at 0 K. The linear expansion coefficient and volumetric coefficient are related by $\alpha = \beta/3$.

3. Results and discussion

3.1. Pressure-induced structural changes

The optimized cell constants are in good agreement with the corresponding experimental values. The thermodynamically stable crystal structure requires the formation enthalpy to be negative. In

this calculation, the obtained value is -0.94 eV/atom, which is similar to the assessed datum -1.03 eV/atom from Ma et al. [8]. The energy–volume values for the different lattice parameters (at constant b/a and c/a) were calculated using the full relaxed atomic position in each step. The calculated $E(V, T) - V$ points were then fitted by means of Birch–Murnaghan’s equation of state (Eq. (1)) at temperature T , as shown in Fig. 2a. It can be observed that as temperature increases, the total energy decreases continuously. The equilibrium volume of Ti_3B_4 increases with the raising temperature (Fig. 2b), which proves the nature of its thermal expansion and contraction. Meanwhile, the bulk modulus and its pressure derivative were estimated based on the same Murnaghan’s EOS. Then, the pressure–volume relationship will be obtained, which will be discussed in next section.

$$E(V) = \frac{B_0 V_0}{B'_0} \left[\frac{1}{B'_0 - 1} \left(\frac{V}{V_0} \right)^{(1-B'_0)} + \frac{V}{V_0} + \frac{B'_0}{1 - B'_0} \right] + E_0 \quad (1)$$

In order to provide some pressure-induced structure information of Ti_3B_4 , both the cell parameters and atomic positions were fully relaxed under pressure from 0 GPa to 36 GPa. The pressure dependence of relative lattice parameters a/a_0 , b/b_0 , c/c_0 , and V/V_0 were obtained and shown in Fig. 3a, where a_0 , b_0 , c_0 , and V_0 are the zero temperature/pressure cell lattice parameters, respectively. From Fig. 3a, all ratios decrease continuously with increasing pressure. The crystal structure along b -axis is slightly less compressible than that along the other axes. When the applied pressure is up to 36 GPa, the b axis length is shortened by about 5%, and finally the volume of Ti_3B_4 cell decreases about 12% of primary structure. The lattice compressibility may be closely related to the layered crystal structure of Ti_3B_4 along [010] direction; the strong chemical bonds exist intra-layer, which are stronger than the bonds between the layers. In Ti_3B_4 crystal cell, boron atoms form a layered sub-lattice by sharing the valence electrons through sp^2 hybridization; the Ti–B bond between each layer is the mixture of ionic–covalent interactions, which is relatively weaker than B–B bond [18–21]. These electronic characters are the main reason for the compressibility anisotropy. Fig. 3b illustrates the relative volumes (V/V_0) of Ti_3B_4 at different pressures and temperature, from which we can see that the relative volume in higher temperature is larger than that in lower temperature under the same pressure; as a given temperature, the relative volume decreases by increasing pressure. In other words, the volume expansion behavior is affected both by temperature and pressure; the former one has positive effect, while

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