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Density functional theory insights into ternary layered boride MoAlB

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ABSTRACT

Density functional theory is used to provide theoretical insights into the ternary nanolaminated and layered transition metal boride (MAB phase) of MoAlB, with calculations of crystal structure, electronic structure, lattice dynamics and elastic properties, including a corresponding hypothetical MAX phase compound Mo_2AlC for comparison. The calculated atomic configuration matches well with experiment. The metal-like electronic structure contributes to the physical origin of the high electrical conductivity of MoAlB. Strong covalent bonding is present between the B atoms, as well as between the Mo and B atoms, and significantly the much weaker Al–Al bonds are consistent with the high fracture toughness and damage tolerance seen in MoAlB. With increasing pressure, the shrinkage is highest along the b axis, and lowest along the c axis. From the calculated second-order elastic constants, the bulk moduli B, shear moduli G, Young's moduli E and Poisson ratio μ are 207 GPa, 137 GPa, 336 GPa and 0.23, respectively. The G/B ratio of 0.66—similar in magnitude to values in MAX phases –demonstrate similarities in properties between MAB and MAX phases. Lattice dynamics are examined in detail, with 9 Raman-active modes and 6 infrared-active modes identified and analyzed in terms of their atomic motion and wavenumbers.

1. Introduction

Binary transition metal carbides (TMCs), nitrides and borides are among the hardest and most refractory materials [1]. Moreover, a unique combination of mechanical, electronic, optical and thermal properties is present in many of them, suggesting these compounds can be used for important engineering applications, such as wear resistant coating, primary battery electrodes, chemical catalysis, and high-temperature structural materials. However, these uses usually suffer from high processing costs, low fracture toughness, low damage tolerance and, more importantly, poor oxidation resistance when heated in air. In an effort to address these limitations, recent research has focused on introducing A-group elements into binary TMCs to form ternary layered carbides and nitrides called M_nAX_{n+1} phases (MAX for short, where M is an early transition metal, A is a group IIIA or IVA element, X is C and/or N, and $n = 1–3$) [2,3]. MAX phases have attracted much attention over the last two decades because of their combination of ceramic- and metal-like properties [4]. Of particular importance, high oxidation resistance has been experimentally observed in some Al-containing MAX carbides including Ti_2AlC [5,6], Ti_3AlC_2 [7,8], and Cr_2AlC [9].

Because of their high melting points, some binary transition-metal borides such as ZrB_2 and HfB_2 – belonging to the class of ultrahigh-temperature ceramics (UHTCs) [10,11] – hold great promise. However, they suffer from intrinsic brittleness, e.g. low fracture toughness and damage tolerance, and poor oxidation resistance. The unique properties of the MAX phases suggest a strategy to improve the intrinsic brittleness and poor oxidation resistance of binary borides by inserting Al layer/s to form nano-laminated, ternary transition-metal borides called “MAB” phases [12]. Like the well-known MAX phases, MAB phases consist of a transition metal boride sublattice interleaved by a monolayer or bilayer of pure Al atoms. Although some studies have been conducted on MAB phases, most of them have focused on single-crystal growth and determination of the crystal structure, as in a recent report on M_2AlB_2 (M = Cr, Mn, Fe) and MAlB (M = Mo, W) [12]. As an exception, Fe_2AlB_2 has attracted much attention recently because of its magnetic phase transition around 304 K, which

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makes it a prospective magnetocaloric material [13,14].

Historically, the discovery and development of new materials has usually been performed in a trial-and-error manner, however, with the disadvantages of high cost and low efficiency. The rapid development of computer hardware and computational methods over the last two decades has provided a powerful means to explore the structures and properties of materials at the atomic scale, which has greatly increased and improved the reliability of theoretical input as a guide to experimental work. For instance, in the field of MAX phases [15–24], significant theoretical investigations using density functional theory (DFT) have been conducted, and have contributed to understanding and predictions of phase stability, lattice parameters, electronic structure, compressibility, phonon related properties, and optical and elastic properties. Overall, the ultimate aim of these theoretical works, conducted mainly using DFT, is to predict properties and lead experimentalists to new compounds with potentially extraordinary properties, as has been demonstrated in the research on MAX phases [25–29]. Recently, inspired by these successes, we applied density functional theory to research the properties of four ternary compounds ($Hf_2Al_3C_4$, $Hf_3Al_3C_5$, $Hf_2Al_4C_5$, and $Hf_3Al_4C_6$) in the Hf–Al–C system [30].

Kota et al. [31] recently synthesized and characterized a dense, predominantly single-phase sample of an MAB-phase compound, MoAlB, using a reactive hot pressing method at 1200 °C for 1 h under a stress peaking at 39 MPa. Importantly, MoAlB was found to exhibit some interesting properties, such as oxidation resistance, high-temperature stability, relatively low hardness and high damage tolerance, rendering it applicable for potential UHTC applications. To respond to this experimental progress, it is important and timely to provide some theoretical insights to better understand the origin of the experimental results and to guide the prediction of its properties. In the present work, the crystal structure, electronic structure, compressibility, and elastic properties of MoAlB are investigated within the framework of DFT. In some cases, a corresponding hypothetical MAX phase compound Mo_2AlC is included for comparison, which shows the similar and different properties between the MAB and MAX phases. These results, in turn, contribute to a better understanding of the MAB phases for potential engineering applications.

2. Theoretical details

2.1. General set and geometrical optimization

The Cambridge Sequential Total Energy Package (CASTEP [32]) code using a plane-wave pseudopotential total energy calculation method based on DFT [33] was employed for all the calculations. After careful convergence tests, the plane-wave energy cutoff and the Brillouin zone sampling were fixed at 450 eV and a $9 \times 2 \times 9$ special *k*-point mesh respectively to ensure total energy convergence to within ±1 meV/atom. The Vanderbilt-type ultrasoft pseudopotential [34] was used to model the interactions of the electrons with ion cores. The electronic exchange-correlation energy was treated according to the Perdew-Wang generalized-gradient approximation (GGA-PW91) [35] and local density approximation (CA-PZ) [36]. The crystal structures (Fig. 1) were fully optimized by independently modifying the lattice parameters and internal coordinates, using a Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimization scheme [37] to minimize the total energy, internal forces and external stresses. Tolerances were set to ensure the convergence of the total energy to within $\pm 5 \times 10^{-6}$ eV/atom, ionic Hellmann-Feynman force components to less than 0.01 eV/Å, ionic displacements converged to within $\pm 5 \times 10^{-4}$ Å and the stress tensor components converged to less than 0.02 GPa.

The electron density difference produces a density difference field which shows the changes in the electron distribution that are due to formation of all the bonds in the system. It is appropriate for bulk solids to illustrate the charge redistribution due to chemical bonding. In practice, this electron density difference can be calculated automatically within the Materials Studio software by taking the electron density of a compound or structure and subtracting from it the corresponding density of the isolated atoms.

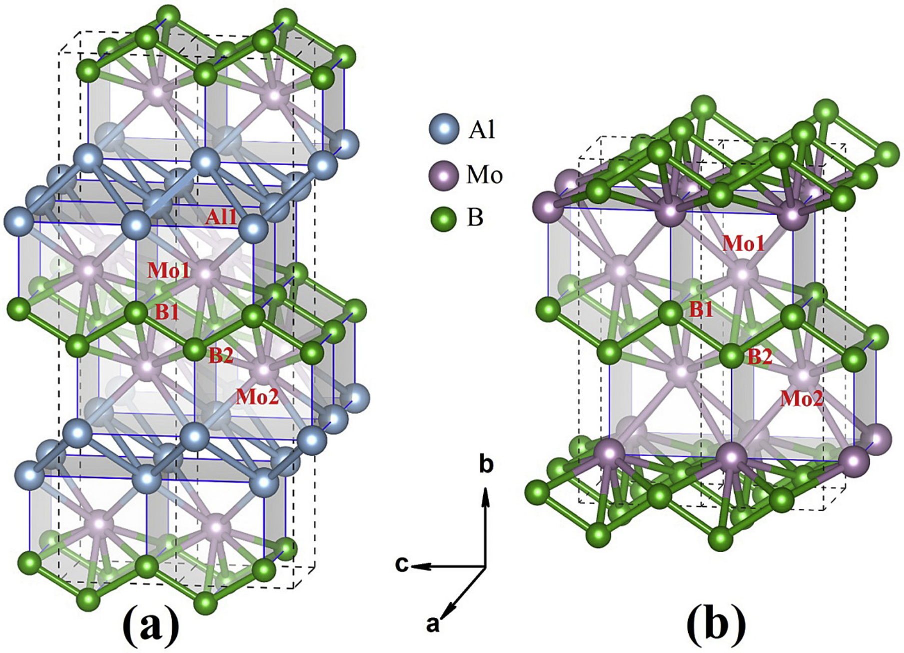

Fig. 1. Crystal structure of (a) MoAlB and (b) MoB. Crystallographically, MoAlB can be regarded as MoB with Al bilayers inserted along the b-direction.