Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 41 (2015) 6831–6843

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

# Structural, anisotropic elastic and thermal properties of MB (M = Ti, Zr and Hf) monoborides

Bo Huang[a], Yong-Hua Duan[a,b,*], Wen-Cheng Hu[c], Yong Sun[a,b], Shuai Chen[a]

[a]School of Material Science and Engineering, Kunming University of Science and Technology, Kunming 650093, China
[b]Key Lab of Advance Materials in Rare & Precious and Nonferrous Metals, Ministry of Education, China, Kunming 650093, China
[c]School of Mechanical and Electrical Engineering, Nanchang University, Nanchang 330031, China

Received 29 December 2014; received in revised form 23 January 2015; accepted 27 January 2015
Available online 3 February 2015

**Abstract**

To better clarify and understand the applications of the transition-metal monoborides, first principles calculations were performed to investigate the structural properties, phase stability, elastic properties, and thermal conductivity of NaCl-type, FeB-type and CrB-type MB (M = Ti, Zr and Hf) monoborides. The results of equilibrium structures, cohesive energies and formation enthalpies are in good agreement with available experimental and other theoretical data. Based on the elastic constants, the polycrystalline elastic properties including bulk modulus, shear modulus, Young's modulus and Poisson's ratio, are obtained by Voigt–Reuss–Hill approximation. All these monoborides are mechanically stable. The elastic anisotropies of monoborides are investigated via the various anisotropic indexes and the 3D surface constructions, and the order of elastic anisotropy is NaCl-type > CrB-type > FeB-type. By using the Cahill's model, the minimum thermal conductivities of these monoborides were also investigated, and the results indicate that the minimum thermal conductivities show a dependence on direction.


*Keywords:* C. Thermal conductivity; Elastic anisotropy; First-principles calculations; Monoborides; Stability

## 1. Introduction

The transition-metal borides, an important family of non-oxide ceramics, are great of interest for structural and functional applications due to their high strength [1,2], superhardness [3,4], superconductivity [5,6], high ferromagnetism [7], high melting point, thermodynamic stability, and resistance to attack by molten metal and glass. As a kind of the transition metal borides, MB (M = Ti, Zr and Hf) monoborides whiskers play a reinforced role in various M-matrix alloys, especially in Ti matrix alloys [8–10]. As the nanocrystalline structure MB monoboride is formed in the primary crystallization reaction from the amorphous phase, much attention has been paid to the mechanism of the nanocrystalline structural evolution in these alloys [11].

MB (M = Ti, Zr and Hf) monoborides have several different crystal structures. A NaCl-type face-centered cubic (FCC) structure with *Fm*-3*m* space group for TiB, ZrB and HfB has been reported [12–16]. The unit cell of NaCl-type MB monoboride contains four MB formula units and B atoms occupy 4a-sites at origin while M atoms situate 4b-sites at (1/2, 1/2, 1/2). The NaCl-type structure ZrB is thermal stable in the temperature range 1073–1523 K [13], even at room temperature after slow cooling [17–19]. Furthermore, TiB and HfB also crystallize in FeB-type structure with a primitive orthorhombic (*Pnma*) crystal belonging to the *mmm* point group [16,20]. It is doubtful for the existence of the FeB-type structure ZrB. There is no ZrB isotypic with the stable FeB-type phase in the investigations from 99.9% pure metal and boron powders [21,22]. By use of the equilibrium phase diagram data for zirconium-borides, the stability or better the instability of ZrB with the FeB-type (isotypic with TiB) has

*Corresponding author at: School of Material Science and Engineering, Kunming University of Science and Technology, Kunming 650093, China. Tel.: +86 871 65136698; fax: +86 871 65136698.
*E-mail address:* duanyh@kmust.edu.cn (Y.-H. Duan).

http://dx.doi.org/10.1016/j.ceramint.2015.01.132
0272-8842/

been estimated [23]. In a further report, ZrB with a FeB-type structure is energetically more stable than the NaCl-type ZrB [24]. For HfB, the FeB-type is a more stable than NaCl-type [16]. The CrB-type structure is usually considered as a distorted version of the FeB-type structure. Thereby another CrB-type orthorhombic structure with *Cmcm* space group for TiB, ZrB and HfB, which is unconfirmed by experiments, is supposed by Xu et al. [25]. In the CrB-type structure MB (M=Ti, Zr and Hf) monoborides, the arrangements of M and boron atoms occupy 4c-sites at (0, 0.146, 0.25) and (0, 0.44, 0.25), respectively, and the boron atoms are in very close contact with one another and each boron atom has two nearest neighbor boron atoms.

Owing to their outstanding physical properties, MB (M=Ti, Zr and Hf) monoborides have been investigated extensively in recent years. The elastic properties and formation enthalpy of FeB-type TiB have been calculated by using the density functional theory (DFT) [9,26–29]. There are different in the theoretical results of elastic constants among the reported literatures. One possible reason is that the lattice constants *a*, *b* and *c* of FeB-type TiB vary from 6.090 to 6.120 Å, from 3.030 to 3.060 Å and from 4.550 to 4.570 Å, respectively. Within the uncertain values of lattice constants, the calculated elastic constants of TiB can change by as much as 10 GPa and even 20 GPa for $C_{66}$. There are no reports associated with the mechanical properties and electronic structures for FeB-type ZrB and HfB. Only the formation enthalpy for FeB-type ZrB is calculated and the values are −79.3 [23], −67.1 or −72.6 kJ/mol [24]. The formation enthalpy of NaCl-type TiB is larger than that of FeB-type TiB, indicating that orthorhombic TiB is more stable than cubic TiB [28]. Although the elastic properties of NaCl-type ZrB have been investigated [30], the important elastic anisotropy, which is closely related to the possibility of inducing micro-cracks in materials, is still lack. As for the CrB-type MB (M=Ti, Zr and Hf) monoborides, the elastic properties, chemical bonding and electronic properties have been investigated by using the ab initio calculations [25]. However, the scarce systematic information of mechanical properties in the MB (M=Ti, Zr and Hf) monoborides hinders the better understandings and applications of these transition-metal borides.

The present work aims to investigate the stabilities (cohesive energy and formation enthalpy), mechanical properties (elastic constants, elastic modulus, hardness and anisotropy) and thermal property (thermal conductivity) of the NaCl-type and FeB-type MB (M=Ti, Zr and Hf) monoborides using the first-principles calculations. For a comparison, the CrB-type structure monoborides are also investigated. This paper is organized as follows. In Section 2 the computational models and details based on the first-principles calculations are depicted. In Section 3 the structural properties, phase stabilities, mechanical properties, elastic anisotropy, and thermal conductivities for MB (M=Ti, Zr and Hf) monoborides are presented. Finally, in Section 4 the conclusions of the present work are given.

## 2. Methods and computational details

The first-principles calculations were performed in present work based on the density functional theory (DFT) [31] using the Cambridge sequential total energy package (CASTEP) code [32]. The interactions between ionic core and valence electrons were represented by the ultrasoft pseudo-potentials (USPPs). Exchange-correlation energy was described by generalized gradient approximation (GGA) of the Perdew–Burke–Ernzerhof (PBE) parameterization [33]. The valence electrons treated in this work were Ti ($3s^2 3p^6 3d^2 4s^2$), Zr ($4s^2 4p^6 4d^2 5s^2$), Hf ($5d^2 6s^2$) and B ($2s^2 2p^1$). The change of total energy during the optimization was converged to $1 \times 10^{-6}$ eV and the force per atom was reduced to 0.02 eV/Å. The Broyden–Fletcher–Goldfarb–Shannon (BFGS) algorithm was applied to relax the crystal structure to reach the ground state where both cell parameters and fractional coordinates of atoms were optimized simultaneously. Brillouin zone (BZ) integrations were performed using Monkhorst–Pack [34] *k*-point meshes. The *k* point separation in the Brillouin zone of the reciprocal space was $10 \times 10 \times 10$, $6 \times 12 \times 8$ and $8 \times 4 \times 10$ for NaCl-type, FeB-type and CrB-type MB monoborides, respectively. The cutoff energy for plane wave expansions was determined as 500 eV. The separation of the reciprocal space was around 0.01 $Å^{-1}$ and the self-consistent field (SCF) tolerance was set as $5 \times 10^{-7}$ eV/atom. With the chosen plane-wave cutoff energy and *k*-point sampling, the total energy is estimated to be converged to a precision of better than 1 meV/atom.

## 3. Results and discussion

### 3.1. Structural properties and stability

The crystal structures of NaCl-type, FeB-type and CrB-type MB (M=Ti, Zr and Hf) monoborides are illustrated in Fig. 1. The information on the atomic positions of FeB-type ZrB adopts those of FeB-type TiB [24]. The lattice parameters of FeB-type ZrB are assumed to apply those of FeB-type HfB due to the close atomic radii of Zr and Hf. The optimized lattice constants and the corresponding experimental and theoretical values for each structure are listed in Table 1. In general, the calculated lattice parameters of these monoborides are in good agreement with the available results. The average deviation of our results to experiments (except NaCl-type structure) and other theoretical results for lattice parameters is about 1%, indicating that the computational method employed in present work is workable and reliable. The calculated structures are slightly more expanded than the experimental ones due to the inherent nature of the GGA approximation. For NaCl-type MB, all the calculated lattice constants are slightly larger than the experiment values, and there are no other available reported experiment values to be compared. However, the present results for NaCl-type ZrB monoborides agree well with the other theoretical calculations [30]. Therefore, the optimized structural parameters for cubic ZrB and HfB should be acceptable. According to the calculated results of FeB-type and CrB-type monoborides, we suppose that our theoretical values $a=4.900$ Å and $a=4.855$ Å for cubic ZrB and HfB, obtained by GGA–PBE method, may be more accurate.

The cohesive energy and formation enthalpy have been calculated to estimate the chemical stability of MB (M=Ti, Zr