Universal Phase Transitions of AlB₂-Type Transition-Metal Diborides

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ABSTRACT: High-pressure phase transitions of AlB₂-type transition-metal diborides (TMB₂; TM = Zr, Sc, Ti, Nb, and Y) were systematically investigated using first-principles calculations. Upon subjecting to pressure, these TMB₂ compounds underwent universal phase transitions from an AlB₂-type to a new high-pressure phase tP6 structure. The analysis of the atomistic mechanism suggests that the tP6 phases result from atomic layer folds of the AlB₂-type parent phases under pressure. Stability studies indicate that the tP6-structured TiB₂ phase may be recovered at ambient pressure.

1. INTRODUCTION

Transition-metal diborides (TMB₂) are attracting considerable research attention due to their unique combination of properties, such as high melting point, hardness, chemical stability, high thermal conductivity, low electrical resistivity, and low work function.¹−⁶ TMB₂ typically crystallizes in the well-known hexagonal AlB₂-type structure (P6/mmm, Z = 1) in which coplanar graphite-like B layers alternately exist with close-packed TM sheets. Many experimental and theoretical studies are focusing on these materials.⁷−⁹ For example, TiB₂ and ZrB₂ have been reported as two prototype materials for the study of the topological nodal-net structure,⁹ TiB₂ is also a candidate material for the development of lightweight high-temperature structural materials,¹⁰ and MgB₂ is a metal-compound superconductor with the highest critical temperature.¹¹

High-pressure research is leading to the discovery of novel behaviors of solids and potential technological materials. Pressure can significantly alter the electron-bonding state to modify the physical properties and/or subsequently induce structural phase transition. However, experimental studies on the phase transition of AlB₂-type TMB₂ compounds are currently rare, and no significant results have been obtained. High-pressure experiments have been performed on HfB₂ up to 30 GPa,²² ZrB₂ and VB₂ up to 50 GPa,²³ and TiB₂ up to 65 GPa,²⁴ and some related mechanical characteristics have been investigated; however, no obvious phase transitions have been observed in any of these compounds. Thus, the stabilities of AlB₂-type TMB₂ seem unshakable, and the high-pressure phases of TMB₂ are yet to be determined.

The difficulty in experimentally identifying high-pressure phases of TMB₂ has stimulated theoretical studies. At very high pressures, performing experiments may be very difficult, but calculations can be easily performed and will provide inspiration for future experimental research, which is also one of the important meanings for computational material science. Thus, calculations can be used to predict new high-pressure phases. Ma et al.²⁵ first theoretically studied a nonsuperconducting high-pressure orthorhombic KHg₂-type polymorph (Imma; Z = 4) of MgB₂ that is stable at >190 GPa through ab initio evolutionary simulations. The thermodynamic properties of TiB₂,²⁶ and the elastic and electronic properties of NbB₂,²⁷ under pressure have also been calculated, and results do not suggest structural transformations over a wide range of pressure (0−200 GPa). Zhang et al.²⁸ presented extensive structure searches to uncover the high-pressure structures of TMB₂ (Sc, Ti, Y, and Zr) up to 300 GPa using the ab initio evolutionary algorithm. They predicted that monoclinic C2/m phases of ScB₂ and YB₂ are stable above 208 and 163 GPa, respectively. A tetragonal α-ThSi₂-type structure of TiB₂ has also been uncovered at 215 GPa, whereas ZrB₂ persists up to 300 GPa within an ambient-pressure AlB₂-type structure. At present, diamond-anvil cells (DACs) can generate pressure beyond 400 GPa²⁹−₃₁ (with a record claimed to exceed 1 TPa). These findings motivated us to continue exploring the phase transitions of AlB₂-type TMB₂ under higher pressure.

In the present work, the high-pressure (up to 800 GPa) phase transitions of AlB₂-type TMB₂ (TM = Zr, Sc, Ti, Nb, and Y) were systematically investigated using first-principles...
The phase-transition mechanism of ZrB2, as a representative simulations at 800 GPa identiﬁed to explore higher-pressure phases. Our evolutionary standing of AlB2-type TMB2 high-pressure transitions and further studied. This study may enrich the common understanding of AlB2-type TMB2, was systematically examined. The stabilities of the new phases of TMB2 were proposed for both ScB2 and YB2 at high pressure but with more relative slip between the B and TM atom layer. Moreover, the wrinkled B layer comprised quadrangle B rings and not hexagonal B rings. Intriguingly, the TM atom naturally fell in the middle of the pocket comprising four quadrangle B rings. Clearly, such tight structural features of the tP6 phase were due to high pressure.

After full optimizations of all proposed structures (see the Computation Methods section for details of structural production), only 8 structured ZrB2 (i.e., AlB2-type,7 the proposed tP6, α-TiB2-type,32 β-TiB2-type,32 hR18,33 hP6,33 oP6,33 and hR933) retained their initial crystal structures; the others (KHg2-type,25 hP12,33 oP12,34 and C2/m28) were either distorted or changed to other structures under the given pressure ranges. ZrB2 persisted up to 800 GPa within an ambient-pressure AlB2-type structure because no new low-energy phase occurred within this pressure range, consistent with previous research.23,28,35 Figure 2 shows that six structured ZrB2 always had higher enthalpies than the AlB2-type phase under the considered pressures, and only one high-pressure phase-transition route was found. For pressures over 800 GPa, the tP6 structure became the most stable phase. The transition pressure points can be distinguished from 350 to 1480 GPa in Figure 3 due to different TM atoms. Although the results of thermodynamic calculations cannot fully represent the experiments, their trends are meaningful.36 These high-transition pressures also explained why no high-
pressure phase transition of TMB$_2$ was found in the experiments within 70 GPa. These phase transitions were all first order due to the significant volume reduction (Figure 3b).

To analyze the phase-transition mechanism, we need to understand the difference in atomic coordination before and after phase transition. The coordination polyhedrons for the TM and B atoms of the AlB$_2$-type and tP6 phases are plotted in Figure 4. High-pressure phase transitions resulted in a significant disruption of symmetry in the corresponding coordination polyhedron. Central atoms of the coordination polyhedral were pushed aside from the AlB$_2$-type phase to the high-pressure phase tP6 structure. Therefore, the B atom in the tP6 phase had two different Wyckoff positions (B1 and B2 shown in different colors in Figure 4). In addition, many coordination polyhedrons with a square pyramid shape appeared due to atomic centrifugation. The most obvious feature was that the coordination atom numbers in the AlB$_2$-type phase were 6TM and 12B for the TM atom and 3B and 6TM for the B atom, whereas in tP6 phase, they were all four atoms (4TM, 4B1, and 4B2) for TM and B atoms.

A similar high-pressure structural rearrangement occurs in TMB$_2$, so understanding the phase-transition mechanisms is very important. Experimental information about the actual path by which a transition occurs is very difficult to obtain, but first-principles calculations also allow investigations of transition paths. As shown in Figure 5, the mechanisms involved atomic displacement and lattice deformation under pressure. The lattice deformation was obviously anisotropic. Lattice $a$ was compressed by 40.6%, lattice $c$ increased by 56.0%, and lattice $b$ was almost unchanged during the phase transition.

Figure 3. (a) Computed enthalpy differences and (b) equations of state for TMB$_2$ compounds along the AlB$_2$ → tP6 phase-transition route.

Figure 4. Coordination polyhedron for the TM and B atoms of the (a) AlB$_2$-type and (b) tP6 phases. The green polyhedron is for TM atoms; purple and pink polyhedrons are for B1 and B2 atoms, respectively.

Figure 5. Compressed phase conversion from AlB$_2$-type to tP6 in ZrB$_2$ compounds under 800 GPa. AlB$_2$-type: a redefined orthorhombic lattice in $P6/mnm$ symmetry containing two ZrB$_2$ formulas; tP6: a tetragonal structure in $P4/nmm$ symmetry containing two ZrB$_2$ formulas. The top, middle, and bottom panels reveal the AlB$_2$-type to tP6 transition path viewed along the $b$, $c$, and $a$ directions, respectively.
mechanically stable at the ground state, whereas those of NbB$_2$ and YB$_2$ were mechanically stable above 100 and 400 GPa, respectively. The bulk and shear moduli of the five AlB$_2$-type TMB$_2$ compounds were also calculated at ambient pressure. The simulated values were compared with available experimental data, and results validated our computational scheme (Table S2 in the Supporting Information).

The dynamical stabilities of the tP6-structured TMB$_2$ were further evaluated. The ZrB$_2$ phase at 20 and 800 GPa, ScB$_2$ phase at 50 and 600 GPa, TiB$_2$ phase at 0 and 1500 GPa, and NbB$_2$ phase at 200 and 1500 GPa had no imaginary phonon frequency within the entire Brillouin zone, that is, these structures are dynamically stable (Figure S1 in the Supporting Information). However, the tP6-structured YB$_2$ phase was found to be dynamically unstable over the entire studied pressure range. These stability results indicated that the tP6-structured ZrB$_2$, ScB$_2$, and NbB$_2$ were stable and exist under high pressure like the KHg$_2$-type MgB$_2$ and that the tP6-structured TiB$_2$ phase may be recovered at ambient pressure. The lattice parameters of the tP6 phases of TMB$_2$ were calculated in view of their possible existence under high pressure. Results are listed in Table S3.

3. CONCLUSIONS

An overall report on the high-pressure phase transitions of AlB$_2$-type TMB$_2$ is presented. Details on the changes in enthalpy, volume, and atomic coordination numbers from the initial phase to the final phase, atomistic mechanism of the phase-transition process, and stabilities of the new phases are included. Unlike in the phase transitions of other AlB$_2$-type TMB$_2$, a novel transition route, that is, the AlB$_2$-type $\rightarrow$ tP6 structural transition, is found in ZrB$_2$, ScB$_2$, TiB$_2$, and NbB$_2$. The phase transitions result from the atomic layer folds of the parent AlB$_2$-type phase under high pressure. The atomistic mechanism of the phase transition indicates that a higher pressure in the lattice a direction is more favorable for the phase transition from the AlB$_2$-type to the tP6 structure. Further research on the mechanical and dynamical stabilities shows that the tP6-structured TiB$_2$ phase may be recovered at ambient pressure and that the tP6-structured ZrB$_2$, ScB$_2$, and NbB$_2$ may observe under high pressure. This study may enrich the common understanding of AlB$_2$-type TMB$_2$ high-pressure transitions and provide a DAC experimental scheme to obtain novel TMB$_2$ metastable phases by adjusting sample crystal orientation.

4. COMPUTATION METHODS

Two methods were used to determine the high-pressure structures. The 11 existing structures reported from the experimental and theoretical studies of AlB$_2$-type metal borides were as follows: the tetragonal structures $\alpha$-TiB$_2$ type (SG, I4$_1$/amd) and $\beta$-TiB$_2$ type (SG, P4$_2$/mmc); the orthorhombic structures KHg$_2$ type (SG, Imma), oP12 (SG, Pnma), and oP6 (SG, Pnmm); the hexagonal structures AlB$_2$ type (SG, P6$_3$/mmm), hP12 (SG, P6$_3$/mmm), and hP6 (SG, P6$_3$/mmm); the monoclinic structure C2$\bar{1}$/m (SG, C2/m); the rhombohedral structures hR18 (SG, R-3m) and hR9 (SG, R-3m). The second method used the recently developed evolutionary and particle-swarm optimization algorithms for crystal-structure prediction, and the most stable structures were predicted using the CALYPSO code. Details of the search algorithms and their applications are described in previous reports.

Calculations for structural optimizations, enthalpies, and elastic stiffness constants were implemented in the CASTEP code based on density functional theory. The ultrasoft pseudopotential was used, and the exchange-correlation function was treated by the Perdew–Burke–Ernzerhof form of the generalized gradient approximation. A kinetic cutoff energy of 800 eV and corresponding Monkhorst-Pack $k$ meshes for different structures were then adopted to ensure that the energy converged to less than 1 meV/atom. Structural optimization was performed until the energy change per atom was less than $5 \times 10^{-6}$ eV, the forces on the atoms were less than 0.01 eV/Å, and all stress components were less than 0.02 GPa. The $P$–$V$ curve is obtained by fully optimizing the structure under the given pressure. Phonon calculations were carried out using a supercell approach within the PHONOPY code as implemented in the Vienna ab initio simulation package. The selected calculation parameters were all tested to ensure that energy convergence was less than 1 meV per atom. To validate our computational scheme, benchmark calculations were conducted for the ZrB$_2$ phase. Our calculated lattice parameters of $a = 3.17$ Å and $c = 3.54$ Å well agreed with the experimental results of $a = 3.17$ Å and $c = 3.53$ Å for the AlB$_2$-type ZrB$_2$. The calculated bulk modulus of the AlB$_2$-type ZrB$_2$ was 239.0 GPa, in agreement with an experimental value of 240.1 GPa.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b04260. Calculated elastic constants, bulk moduli $B$, and shear moduli $G$ of the AlB$_2$-type and high-pressure phases of TMB$_2$ at ground state and under high pressure; calculated phonon dispersion curves for the tP6-structured ZrB$_2$ phase at 20 GPa, ScB$_2$ phase at 50 GPa, TiB$_2$ phase at 0 GPa, and NbB$_2$ phase at 200 GPa; ground-state equilibrium lattice parameters for the high-pressure tP6 phases of TMB$_2$ (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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