

J Adv Ceram 2026, **15**: 9221386

<https://doi.org/10.26599/JAC.2026.9221386>

Review

Progress and prospects in MAB phases: A comprehensive review of structure, synthesis, and multifunctional properties

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Abstract

MAB phases comprise a diverse family of layered ternary and quaternary transition-metal borides and related 211-type MAX borides. Conventional MAB phases contain transition-metal–boron structural units separated by A-containing layers; in many Al-containing members, strong M–B and, where present, B–B interactions coexist with relatively weak A-related interactions, producing anisotropic mechanical and transport behavior. Selected MAB phases combine high hardness, damage tolerance, electrical and thermal conductivity, oxidation resistance, crack-healing capability, or radiation tolerance, although these properties depend on composition, structure, phase purity, and processing history. Selected MAB phases can also serve as precursors for topochemical synthesis of two-dimensional MBenes, which have been investigated for energy storage, electrocatalysis, sensing, and optoelectronic applications. This review traces the historical development of the MAB phase field, establishes an operational scope and classification framework for conventional MAB phases and related subfamilies, and describes the structural diversity arising from stoichiometry, crystal symmetry, boron-network topology, and chemical ordering. It surveys computational approaches for evaluating

thermodynamic, dynamical, and mechanical stability and for predicting intrinsic properties, and critically examines experimental synthesis routes for powders, dense bulks, single crystals, thin films, coatings, and selected MBene derivatives. The review further evaluates mechanical, thermophysical, high-temperature, tribological, radiation-related, and functional properties with attention to sample state and measurement conditions. By connecting composition, structure, bonding, processing, and performance, this review identifies both the opportunities and the limitations that must be addressed before MAB phases and MBenes can be translated into practical applications.

Keywords: MAB phases; Nanolaminated transition-metal borides; Damage tolerance; MBenes; Structure–property relationship

1. Introduction

The term “MAB phases” is used here as a broad family designation for layered ternary and quaternary transition-metal borides containing A elements, with conventional members built from transition-metal–boron structural units and A-containing layers [1–3]. In many Al-containing MAB phases, strong covalent M–B and B–B interactions coexist with relatively weak A-related interactions, producing a combination of ceramic-like stiffness and directional compliance. This architecture can promote damage-tolerant deformation through mechanisms such as layer sliding, crack deflection, delamination, and crack bridging, but the dominant mechanism depends on the composition, crystal structure, microstructure, and loading condition [2,4]. Selected MAB phases also exhibit electrical and thermal conductivity,

high-temperature oxidation resistance [5,6], crack-healing behavior [7], radiation-related functionality [8,9], or magnetic and electrochemical responses. In addition, selected MAB phases can serve as precursors for two-dimensional transition-metal borides, or MBenes, although the structure and composition of the resulting derivative depend strongly on the parent phase and the removal process [10,11].

Although the first MAB phase compound, MoAlB, was reported as early as 1942 [12], this system received little attention for several decades thereafter. In 2013, Tan et al. discovered that Fe_2AlB_2 exhibited a significant magnetocaloric effect near room temperature, highlighting its functional value [13]. In 2015, with the explicit proposal of the unified concept of "MAB phases" and the successful preparation of high-quality single crystals [1], this family of materials accelerated research in this field. The subsequent research led to the discovery of numerous MAB phases, revealing their potential for applications as high-temperature structural components [2], wear-resistant [14] and radiation-resistant materials [8], and magnetic refrigeration [13,15]. A key experimental advance in 2018 was the report of an Al-depleted layered CrB product following treatment of Cr_2AlB_2 [10]. This successfully extended the application boundaries of MAB phases to energy conversion and storage fields such as energy storage and catalysis [16–18]. In recent years, through the combination of theoretical prediction and experimental synthesis, novel structures such as in-plane chemically ordered quaternary *i*-MAB phases [11,19,20] and hexagonal *h*-MAB phases [21] have continuously emerged, greatly

enriching the compositional and structural diversity of the MAB phase family. The field has consequently developed an expanding structural taxonomy, an increasingly diverse synthesis toolkit, and a growing portfolio of bulk and two-dimensional applications, while the nomenclature and classification of several related borides remain under discussion.

Despite the expanding phase family, mechanistic understanding, scalable synthesis and practical deployment remain limited. This review connects the history and structural diversity of MAB phases with computational predictions, experimental synthesis, bulk properties and MBene applications, and identifies priorities for further research.

This review uses MAB as a broad family designation for layered transition-metal borides containing A elements. It covers conventional orthorhombic Al-containing phases (e.g., MoAlB , Cr_2AlB_2 , and Cr_3AlB_4), chemically ordered *i*-MAB and *o*-MAB phases, and hexagonal h-MAB phases such as Ti_2InB_2 . Related 512/T2 structures and 211-type MAX borides, including Zr_2SB , Hf_2SB , and Nb_2SB , are included as explicitly identified subfamilies within this broad scope [3,21–24]. Their inclusion reflects structural and compositional relationships, rather than a requirement that every member exhibit weak interlayer bonding, damage tolerance, or demonstrated exfoliation. The classification criteria and the overlap with MAX borides are explained in Section 3.1. Relative to the 2020 review by Kota et al. [3], which focused primarily on Al-containing MAB phases, this review extends the discussion to subsequent developments, including rare-earth-containing ordered phases [25,26],

vacancy-ordered boridene [11], experimentally investigated MBene-based electrocatalysts [27,28], and selected synthesis advances reported through 2026 [29]. It brings bulk MAB properties and MBene synthesis and applications into a common structure–processing–property discussion, compiles calculated elastic properties separately from experimental mechanical and physical data, and compares thermodynamic, dynamical, and mechanical stability assessments without equating computational stability with experimental synthesizability.

Terminologically, “MAB phases” denotes the operational materials-family category adopted in this review, including the explicitly identified related subfamilies described above. By contrast, “nanolaminated transition-metal borides” is a descriptive structural term rather than a strict synonym for MAB phases; it may also refer to layered borides that fall outside the MAB scope used here. The former term is therefore used for the defined phase family, whereas the latter is retained as a broader descriptor of structure and material morphology.

2. Historical Development of MAB Phases

As illustrated in the milestone timeline of Fig. 1, Halla and Thury first synthesized $\text{Mo}_7\text{Al}_6\text{B}_7$ (later identified as MoAlB) in 1942 [12]. Subsequently, during the 1960s, the crystal structures of a series of ternary borides were determined. In 1966, Jeitschko characterized the crystal structure of MoAlB in detail, determining its space group as $Cmcm$ and confirming that it consists of alternative stacking of a CrB-type Mo–B sub-lattice and Al bilayers [30]. In the same year, Becher et al. synthesized Mn_2AlB_2 [31]. Jeitschko reported the crystal structure of Fe_2AlB_2 in 1969

[32]. In 1973, Chaban and Kuz'ma reported Cr_2AlB_2 and Cr_3AlB_4 in their investigation of the Cr–Al–B and Mn–Al–B ternary systems [33]. However, due to the lack of understanding regarding the comprehensive properties of MAB phase compounds at the time, coupled with the difficulty in preparing bulk materials, these compounds were almost completely ignored by the materials science community in the following decades. A notable advance came in 1997, when Okada et al. successfully synthesized high-quality single crystals of $(\text{Mo}_x\text{Cr}_{1-x})\text{AlB}$ and $(\text{Mo}_x\text{W}_{1-x})\text{AlB}$ solid solutions using the metal Al flux method, and systematically investigated their lattice parameters, Vickers hardness, and electrical resistivity [34].

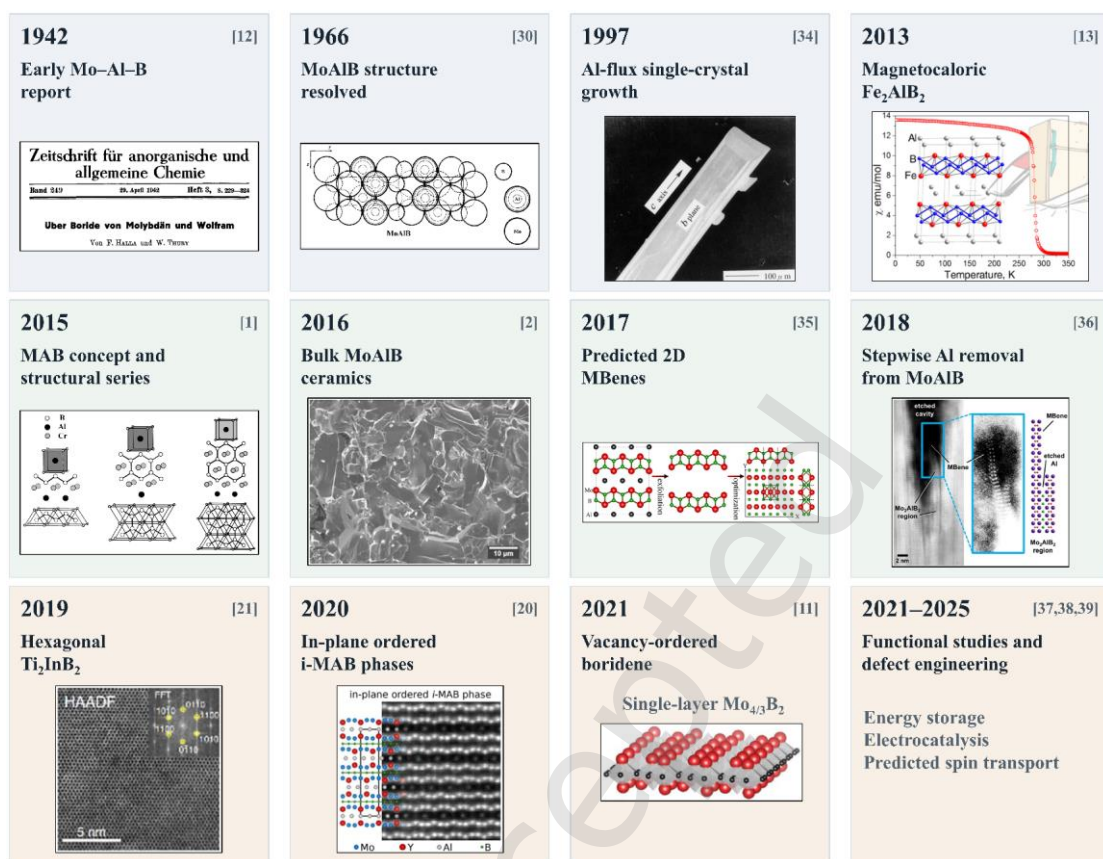


Fig. 1. Selected milestones in MAB-phase and MBene research. Published images illustrate the historical, structural and experimental milestones [1,2,11–13,20,21,30,34–36]; the final node highlights recent functional and computational studies [37–39]. Section 2 distinguishes predictions, synthesized parents and identified derivatives.

Images adapted from Refs. [1,2,11–13,20,21,30,34–36]. The 2013 panel is from the graphical abstract of Ref. [13], and the 2017 panel is from Fig. S3 in the Supporting Information of Ref. [35]. Adapted with permission from Ref. [12] for the 1942 milestone; Ref. [30] for the 1966 milestone, © Springer-Verlag 1966; Ref. [34], © Academic Press 1997; Ref. [13], © American Chemical Society 2013; Ref. [1], © American Chemical Society 2015; Ref. [35], © Royal Society of Chemistry 2017; Ref. [36], © American Chemical Society 2018; Ref. [11], © The Authors 2021, exclusive licensee American Association for the Advancement of Science. Adapted from Refs. [2] and [21], © The Authors 2016 and 2019, respectively, under CC BY 4.0 (<https://creativecommons.org/licenses/by/4.0/>). Adapted from Ref. [20], © American Chemical Society 2020, under CC BY (https://pubs.acs.org/page/policy/authorchoice_ccby_termsfuse.html). Ref. [13] is published under the ACS AuthorChoice License. Images have been cropped and rearranged for this review.

It was not until 2013 that Tan et al. discovered that Fe_2AlB_2 exhibited a significant magnetocaloric effect near room temperature (~ 307 K), making it a potential magnetic refrigeration material [13]. This discovery of functionality,

demonstrating the value of such ternary borides beyond structural applications for the first time, sparked new research interest. In 2015, German scientists Ade and Hillebrecht completed a landmark work [1]. Using elemental powder precursors, they successfully grew a series of high-quality single crystals, including Cr_2AlB_2 , Cr_3AlB_4 , Cr_4AlB_6 , MoAlB , WAlB , Mn_2AlB_2 , and Fe_2AlB_2 . For the first time, they explicitly proposed the unified concept of "MAB phases" (herein M is a transition metal, A is group A element, and B is boron), drawing an analogy with the well-known MAX phases (where M is a transition metal, A is group A element, X is C, N and recently has been extended to also include B). Their work integrated previously disparate individual compounds into a family of materials with common structural features and performance potential, marking the formal entry of MAB phases into the field of materials research.

In 2016, Kota et al. successfully prepared dense polycrystalline bulk MoAlB (relative density $\sim 94\%$) using reactive hot pressing [2]. They reported that polycrystalline MoAlB bulk had a hardness of 10.6 GPa, a compressive strength of 1.94 GPa, a thermal conductivity of $35 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, and remained stable in an inert atmosphere at least up to 1400°C . It also exhibited excellent high-temperature oxidation resistance (due to the formation of a protective dense Al_2O_3 layer). Later, it was demonstrated that MAB phases not only possessed high-temperature oxidation resistance but also exhibited high-temperature self-healing capability [7]. In 2017, Li et al. synthesized Fe_2AlB_2 bulk via hot pressing and experimentally proved its good damage tolerance and non-catastrophic fracture behavior, akin to the MAX phases [4].

These studies established MAB phases as viable high-temperature structural ceramics and stimulated a sustained research effort into their high-temperature behavior.

The prediction of two-dimensional transition-metal borides and the introduction of the term MBenes in 2017 [35] motivated experiments on selective Al removal. Early work on MoAlB and Cr₂AlB₂ identified partially etched structures, intergrowths and local or layered boride products [10,36,40]. Their product identities and evidence for isolated sheets are discussed after the parent phases in Section 5.9.

Furthermore, Zhang et al. subsequently discovered and identified a novel MAB phase compound, Cr₄AlB₄ (the 414-type), through high-temperature reactions, enriching the structural family of MAB phases [41]. In 2019, Dai et al. [42], via high-throughput screening, predicted out-of-plane ordered quaternary MAB phases, abbreviated as *o*-MAB phases. In the same year, Wang et al. theoretically predicted and experimentally synthesized the first *h*-MAB phase, Ti₂InB₂, a ternary layered MAB phase with hexagonal $P\bar{6}m2$ symmetry [21]. In 2020, Dahlqvist et al. [20] introduced a new subclass of quaternary MAB phases in which two transition metals occupy distinct M-sites with in-plane chemical order (*i*-MAB phases). First-principles calculations predicted 15 stable ordered compositions and 16 stable disordered alloys, and bulk Mo_{4/3}Y_{2/3}AlB₂ and Mo_{4/3}Sc_{2/3}AlB₂ were subsequently synthesized to validate these predictions. The structural characteristics and compositional implications of *i*-MAB phases are discussed in detail in **Section 3.1**. Building on this foundation, Zhou et al. [11] selectively etched the Al and Y layers from (Mo_{2/3}Y_{1/3})₂AlB₂ to yield "boridene" (Mo_{4/3}B_{2-x}T_z), a 2D material with ordered metal vacancies whose

electrochemical properties are discussed in **Section 6.6**. This demonstration that *i*-MAB phases can serve as precursors for vacancy-engineered 2D derivatives substantially broadened the application scope of the MAB phase family. The 2021 node in Fig. 1 shows the idealized $\text{Mo}_{4/3}\text{B}_2$ sheet, whereas the experimentally obtained boridene contains nonstoichiometry and surface terminations, as represented by $\text{Mo}_{4/3}\text{B}_{2-x}\text{T}_z$ [11].

Subsequent research has extended from structural ceramics to magnetocaloric response, electromagnetic functions, surface chemistry and electrochemical applications [8,13–16,25,27,37,38,43–59]. These developments involve both bulk parents and identified derivatives, with computational predictions and experimental measurements contributing different kinds of evidence. Examples highlighted in the final node of Fig. 1 include defect-engineered Ti_2InB_2 electrodes [37], calculated HER activity of *h*-MBenes [38], and predicted spin transport in MBene-based device models [39]. The application map and material-specific comparisons are introduced in Section 6.

Intriguingly, MAB phases and MAX phases share a series of similarities. In representative conventional members, A-containing layers separate relatively stiff M–X or M–B structural units. Layered architecture, anisotropic response, damage tolerance, and useful transport properties have been reported in selected compositions; their extent depends on the particular material and testing conditions. In addition, in both MAX phases and MAB phases, solid solutions or ordered phases (e.g., *i*-MAB phases analogous to *i*-MAX phases) can form at the M and A sites. However,

differences also exist between them. For instance, the X element in MAX phases is mainly carbon or nitrogen although it has recently been extended to boron, while the B in MAB phases is only boron; MAX phases are almost exclusively hexagonal (P63/mmc), whereas MAB phases exhibit multiple crystal systems; boron atoms are smaller and have different electronegativity [3,20,21,60]. In borides containing connected B–B units, the structural motifs include alternating stacks of single or double B–B chains, one or two hexagonal B–B rings, or transition metal boride layers with B₆ octahedra and one or two A-group atom layers (primarily Al atom layers) [1,20,21,61]. The comparison in Section 3 draws on the bonding, synthesis and property evidence discussed in Sections 3–6.

The historical progression has connected crystallographic identification with targeted synthesis, property measurements and two-dimensional derivatives. The resulting family now requires complementary composition and structure descriptors, introduced in Section 3, rather than a single universal bonding or performance criterion. Figure 2 summarizes representative structural prototypes before the detailed descriptors in Section 3. Sections 4–6 then connect predicted behavior with preparation and experimental evidence.

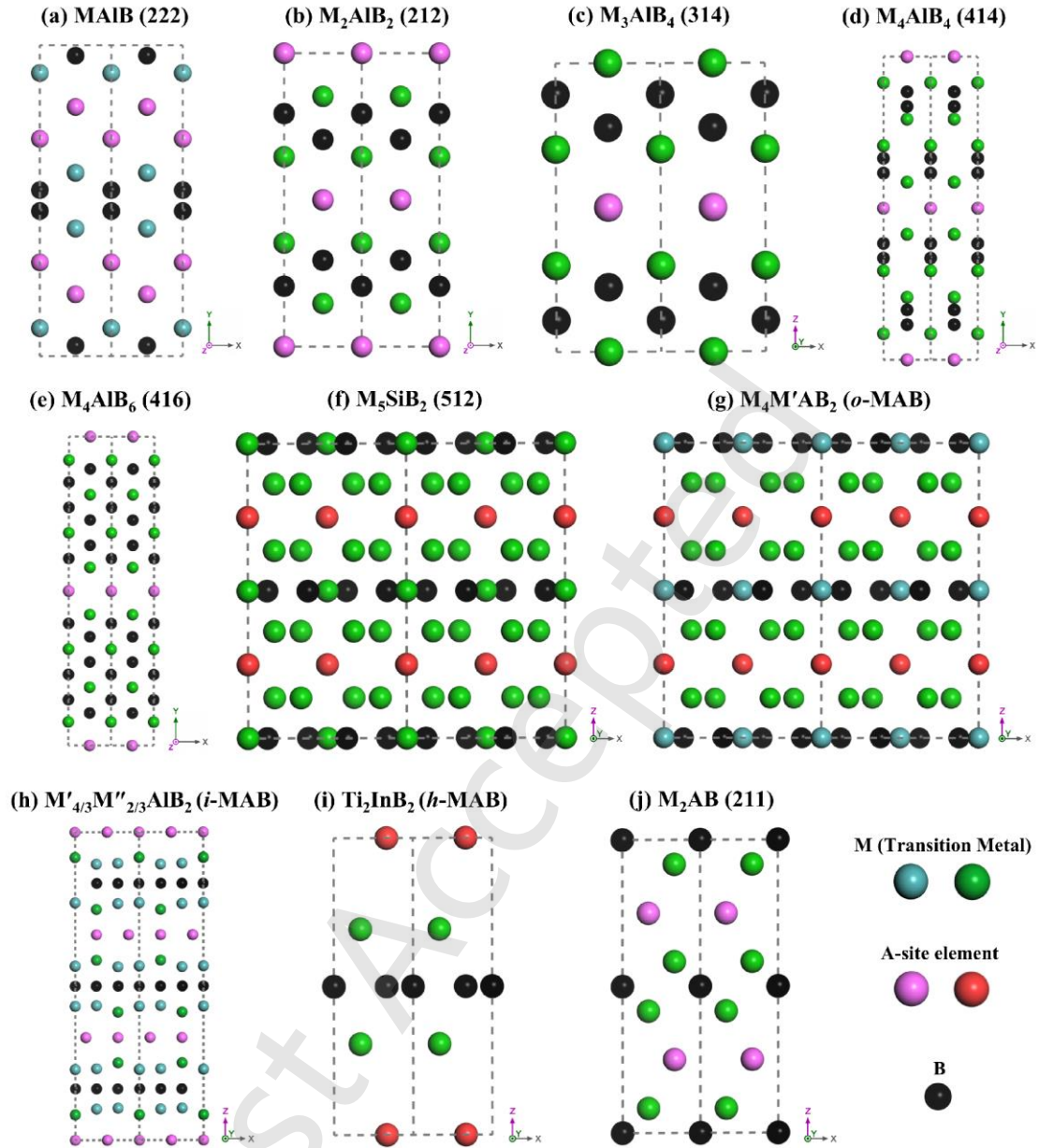


Fig. 2. Representative structural prototypes within the operational scope: (a–e) conventional Al-containing 222, 212, 314, 414 and 416 structures; (f) 512/T2; (g) out-of-plane metal ordering; (h) in-plane metal ordering; (i) hexagonal Ti_2InB_2 ; and (j) related 211-type MAX borides. Purple and red spheres denote A-site atoms; the identity of A depends on the composition. Stoichiometry, symmetry and ordering are complementary descriptors; the models are not normalized to an equal number of atoms. Drawn by the authors from published structural data; see Sections 3.1–3.2.

3. Characteristics and Features of MAB Phases

3.1 Chemical Composition of MAB Phases

Defining the MAB Phase Family: Scope and Classification Criteria. The

original MAB designation describes layered ternary borides built from transition-metal–boron structural units and A-containing layers, initially exemplified mainly by Al-containing compounds [1]. Here, classification distinguishes three intersecting descriptors: chemical stoichiometry (e.g., 212, 314, or 512), crystal symmetry (e.g., orthorhombic or hexagonal), and chemical ordering on the metal sublattice (in-plane *i*-MAB or out-of-plane *o*-MAB). These descriptors are not mutually exclusive structure classes. The expression $(\text{MB})_{2x}\text{Al}_y(\text{MB}_2)_z$ describes much of the conventional orthorhombic Al-containing series, but does not itself specify metal-site ordering and is not a universal formula for the broader family [3]. In this review, experimentally reported structures and explicitly identified predicted candidates are distinguished; related 512/T2 and Zn-containing structures are discussed with their specific structural qualifications (Section 3.2). For the 211-type MAX borides M_2AB , exemplified by Zr_2SB , Hf_2SB , and Nb_2SB , boron occupies the X site of the Cr_2AlC -type MAX structure ($\text{P6}_3/\text{mmc}$) [22,23]. Reports on Zr_2SeB and Hf_2SeB explicitly recognize this overlap between MAX borides and the broader MAB designation [24]. We therefore retain 211-type MAX borides as a distinct, related subfamily within the scope of this review, while recognizing that a narrower use of MAB excludes them. Strong M–B and, where present, B–B interactions relative to selected A-related interactions are useful features of many conventional MAB phases, but their bond hierarchy must be evaluated for the individual composition and structure. Neither a universal B–B network nor identical damage tolerance or susceptibility to A-layer removal is assumed for all included subfamilies.

Early studies of MAB phases included 3d transition metals such as Cr, Mn, and Fe, as well as the 4d metal Mo and the 5d metal W [1]. Subsequent experimental and computational studies expanded the compositional space to include Sc, Ti, V, Nb, Hf, Ta, Zr, and rare-earth-containing ordered phases involving Tb, Dy, Ho, Er, Tm, and Lu [1,20,22,25,62,63]. Within the broad operational scope used here, A identifies the layer species and is not restricted to periodic-table groups 13 and 14. Al is the principal A element in conventional MAB phases, whereas non-Al compositions and related subfamilies studied experimentally or computationally involve Si, Ga, In, Ge, Sn, P, Zn, S, Se, and Te [1,3,22,64 – 66]. The experimental status and structural subfamily of individual examples are specified below. B denotes boron. Based on single-crystal studies of a series of ternary layered borides, Ade and Hillebrecht used the general formula $(MB)_2Al_y(MB_2)_z$ ($y = 1, 2, 3, \dots; z = 0, 1, 2, \dots$) to describe this class of compounds. Their core structural feature is the alternating arrangement of M–B slabs and layers of A elements (mainly Al at the time) [1]. Then, Zhang et al. successfully synthesized Cr_4AlB_4 (414-type), a new MAB phase [41]. The discovery of this structure demonstrates that the general formula proposed by Ade et al. cannot cover all MAB phases. Consequently, the general formula was revised to the extended expression $(MB)_{2x}Al_y(MB_2)_z$ ($x = 1, 2, \dots; y = 1, 2, 3, \dots; z = 0, 1, 2, \dots$) [3]. No single formula currently covers the full structural range.

In addition to the aforementioned MAB phases, recently, Rackl et al. [23] discovered that boron could act as one of the X elements in MAX phases and successfully synthesized the first MAX phase boride, Nb_2SB . They subsequently

reported two other new MAX phase borides, Zr_2SB and Hf_2SB [22]. Furthermore, three other new MAX phases, Zr_2SeB [24], Hf_2SeB [24], and Hf_2TeB [67], were successfully synthesized. As noted in Section 1, MAX phase borides such as Nb_2SB satisfy both the MAX phase definition and the MAB phase description, revealing a structural overlap between the two families [24]; this convergence has motivated the inclusion of 211-type borides within the MAB phase classification.

The introduction of a second transition metal at the M-site opens a distinct compositional pathway: in-plane chemical ordering between two M-site species can thermodynamically stabilize phases that would otherwise adopt disordered solid solutions. As shown in the predicted phase stability diagrams (Fig. 3(a) and (b)), Dahlqvist et al. [20] predicted 15 stable ordered *i*-MAB compositions and 16 stable disordered alloys. The experimental realization of bulk $\text{Mo}_{4/3}\text{Y}_{2/3}\text{AlB}_2$ and $\text{Mo}_{4/3}\text{Sc}_{2/3}\text{AlB}_2$ confirmed these predictions, as verified by TEM and XRD characterizations (Fig. 3(c-g)) [20]. Atomic-resolution HRSTEM imaging and selected-area electron diffraction (SAED) unambiguously visualized the distinct in-plane chemical ordering of the transition metals, as demonstrated for the $\text{Mo}_{4/3}\text{Y}_{2/3}\text{AlB}_2$ system (Fig. 3(c-e)) and the $\text{Mo}_{4/3}\text{Sc}_{2/3}\text{AlB}_2$ system (Fig. 3(g)). This alloying study extended the compositional space to Sc, Y, Zr, Hf, and Nb, which had not previously been used in the ternary counterparts considered in that work [20]. Design guidelines for selecting compatible M-site pairs, based on differences in atomic size and electronegativity, were subsequently formalized by Dahlqvist et al. [19], while Yao et al. [68] extended the same framework to predict 22 stable

quaternary h-MAB phases. The rare-earth series was further expanded by Tao et al. [26], who synthesized $\text{Mo}_{4/3}\text{RE}_{2/3}\text{AlB}_2$ phases with RE = Ho, Er, and Tb, demonstrating that magnetic rare-earth elements can be incorporated at the M''-site through the same ordering pathway. Beyond M-site substitution, parameters such as the number of A-atom planes, the thickness of M–B slabs, and the orientation of B–B chains represent additional compositional and structural variables for exploring new MAB phases [3].

In summary, the chemical formula of MAB phases has undergone successive revisions as new structural types were discovered and the boundary with MAX phase borides was clarified. No single expression currently encompasses all confirmed structural types, reflecting a compositional and structural richness that far exceeds the scope of the original definition.

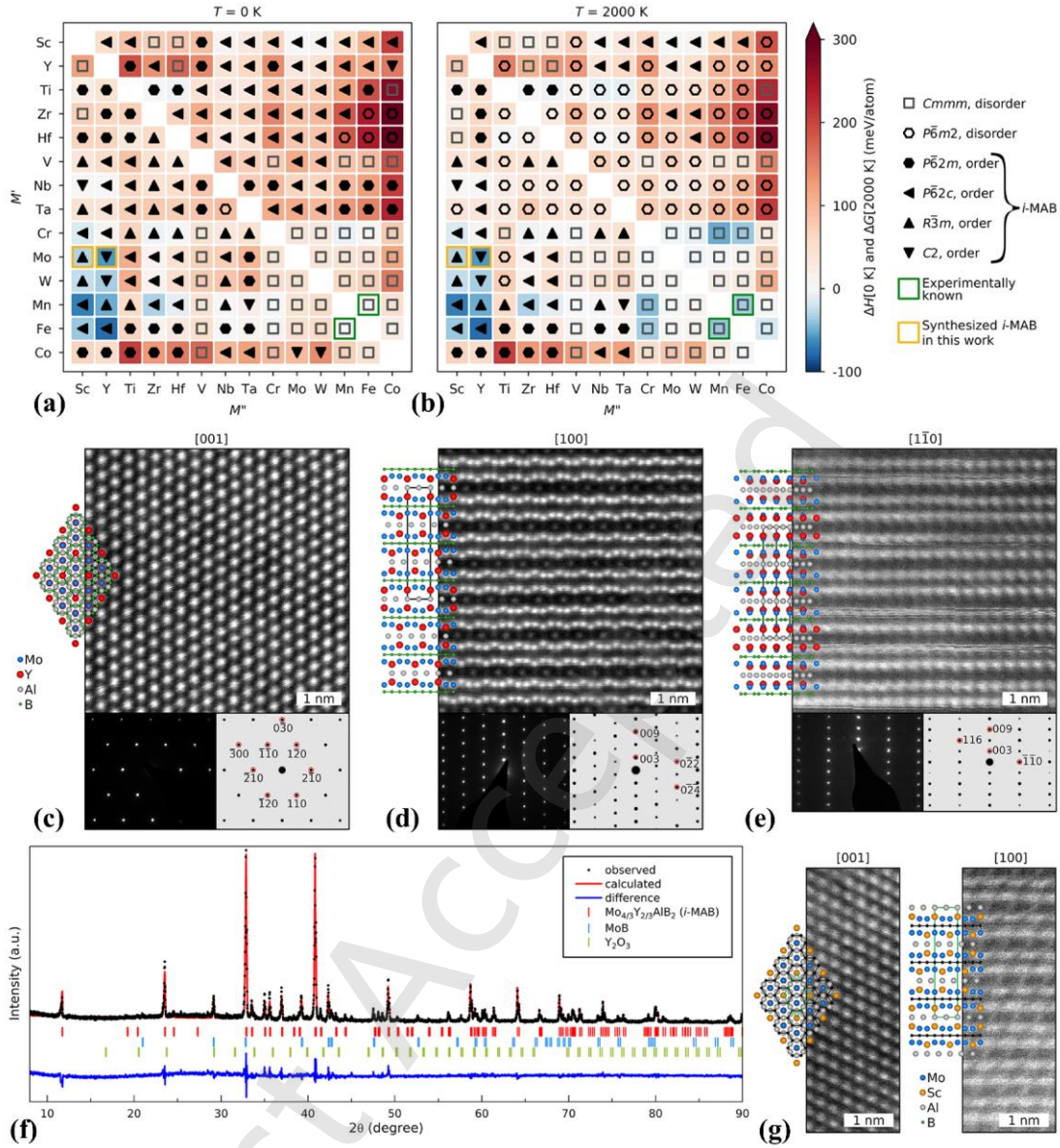


Fig. 3. In-plane chemical ordering in quaternary MAB phases: (a,b) calculated stability of ordered and disordered compositions at 0 and 2000 K; (c – e) HRSTEM, diffraction and structural models of Mo_{4/3}Y_{2/3}AlB₂; (f) XRD refinement; and (g) HRSTEM of Mo_{4/3}Sc_{2/3}AlB₂ [20]. Adapted from Ref. [20], © American Chemical Society 2020, under CC BY (https://pubs.acs.org/page/policy/authorchoice_ccby_termsofuse.html); panels rearranged.

3.2 Structural Features of MAB Phases

The structural prototypes considered here differ in the thickness and topology of their M–B units, A-layer stacking, and chemical ordering (Fig. 2) [3]. In the conventional Cr–Al–B and Mo–Al–B examples, B–B and many M–B interactions

have substantial covalent character, while selected Al-related interactions are more compliant [61,69]. The electronic evidence and the interpretation of polar or metallic contributions are discussed in Section 4.2.1. The primary structure types include:

222-type (also referred to as 111-type or MAIB-type): Chemical formula $MAIB$ (e.g., $MoAlB$, $WAlB$), crystallizing in the orthorhombic $Cmcm$ space group, where M–B slabs are interleaved by double Al atomic layers (Fig. 2(a)) [1,12,30,70,71].

212-type: Chemical formula M_2AlB_2 (e.g., Cr_2AlB_2 , Mn_2AlB_2 , Fe_2AlB_2), crystallizing in the orthorhombic $Cmmm$ space group, featuring M–B slabs separated by a single Al atomic layer (Fig. 2(b)) [1,31,33,72]. Beyond Al-based compounds, theoretical screenings have predicted non-Al 212-type borides with different symmetries, including Si-based variants such as Cr_2SiB_2 and $\alpha-Mo_2SiB_2$ [63].

314-type: Chemical formula M_3AlB_4 (e.g., Cr_3AlB_4), typically crystallizing in the $Pmmm$ or $Immm$ space group, with single Al layers separating the M–B slabs in Cr_3AlB_4 (Fig. 2(c)) [1,73,74].

414-type: Chemical formula M_4AlB_4 (e.g., Cr_4AlB_4 , as well as theoretically predicted Mo_4AlB_4 and W_4AlB_4), crystallizing in the $Immm$ or $Cmmm$ space group (Fig. 2(d)) [41,75,76]. The exact space group assignment for 414-type phases remains a subject of debate, with both $Immm$ and $Cmmm$ reported in the literature.

416-type: Chemical formula M_4AlB_6 (e.g., Cr_4AlB_6), crystallizing in the orthorhombic $Cmmm$ space group (Fig. 2(e)) [1,77].

512-type (also known as the T2 phase, derived from the Cr_5B_3 structure type): Chemical formula M_5AB_2 ($A = Si, Ge, P$, etc.) (e.g., Mn_5SiB_2 , Fe_5SiB_2 , and Mo_5SiB_2),

crystallizing in the tetragonal $I4/mcm$ space group. In this structure, A atomic layers are intercalated within an M_5B_2 framework, rather than between discrete M–B slabs as in the 212–416 series (Fig. 2(f)) [3,78–80].

o-MAB phase (out-of-plane chemically ordered quaternary MAB): Chemical formula $M_4M'AB_2$ (e.g., Ti_4MoSiB_2 , Mo_4CrSiB_2 , W_4CrSiB_2 , Nb_4CrSiB_2 , and Ta_4CrSiB_2), crystallizing in the tetragonal $I4/mcm$ space group. These phases feature an ordered stacking of two different transition metals along the out-of-plane direction within the M-sublattice (Fig. 2(g)) [81,82].

i-MAB phase (in-plane chemically ordered quaternary MAB): Chemical formula $M'_{4/3}M''_{2/3}AlB_2$ (e.g., $(Mo_{2/3}Sc_{1/3})_2AlB_2$, $Cr_{4/3}Y_{2/3}AlB_2$, $W_{4/3}Sc_{2/3}AlB_2$), crystallizing in the trigonal $R\bar{3}m$ space group. Unlike *o*-MAB, the chemical ordering in *i*-MAB occurs within the basal plane — two transition metals (M' and M'') occupy distinct sites in the M-sublattice with a $\sqrt{3} \times \sqrt{3}$ in-plane superstructure (Fig. 2(h)) [83].

h-MAB phase (hexagonal MAB): Nanolaminated ternary borides crystallizing in the hexagonal $P\bar{6}m2$ space group, such as the experimentally synthesized Ti_2InB_2 and Hf_2InB_2 . In contrast to the orthorhombic 212-type phases, *h*-MAB compounds feature flat boron layers rather than the zigzag B-chains characteristic of the $Cmmm$ structure (Fig. 2(i)) [21,84].

211-type MAX borides: Chemical formula M_2AB (e.g., Zr_2SB , Hf_2SB , Nb_2SB , Zr_2SeB , Hf_2SeB , and Hf_2TeB), crystallizing in the hexagonal $P6_3/mmc$ space group. These compounds adopt the prototypical Cr_2AlC -type MAX phase structure with boron occupying the X-site. Whether 211-type borides should be strictly classified as

MAB phases or as a distinct subset of MAX-phase borides remains an open discussion in the literature (Fig. 2(j)) [22–24,67].

Zn-containing compounds provide further examples of distinct boron arrangements. Ref. [66] identified monoclinic C2/m $\text{Ni}_3\text{Zn}_2\text{B}$ and Ni_2ZnB , with isolated B atoms in the former and B–B pairs in the latter. It also related Ni_2ZnB structurally to Ni_3ZnB_2 through removal of a nearly planar Ni layer. These compounds are discussed here as MAB-related borides [3,66] and have structures distinct from the conventional orthorhombic 212 prototype.

Non-Al chemistry also occurs within the 212 and 314 stoichiometries, so those ratios should not be equated with the conventional orthorhombic Al-containing structures. Experimentally synthesized Ti_2InB_2 and Hf_2InB_2 provide hexagonal 212 examples [21,84]. V_3PB_4 is an experimentally reported hexagonal 314 example [28,84], extending the non-Al scope beyond the 212 stoichiometry. Their planar boron sheets differ from the zigzag chains in orthorhombic Fe_2AlB_2 ; the A-layer environment and slab topology therefore change together with chemistry. Miao et al. predicted additional hexagonal 212 candidates, including Hf_2SnB_2 , Zr_2TlB_2 , Zr_2PbB_2 and Zr_2InB_2 , and hexagonal 314 Hf_3PB_4 and Zr_3CdB_4 with thicker metal–boron slabs [85]. These latter compositions were computational candidates in that study.

The property implications likewise require structure-specific evidence. Ref. [21] measured metallic transport in Ti_2InB_2 , whereas the elastic and bonding descriptors of the additional candidates in Ref. [85] were calculated. Selective A removal is not guaranteed by either a planar B layer or favorable bulk stability: Ti_2InB_2 dealloying

produced a reconstructed layered TiB-containing material [21], while molten-salt treatment of Hf_2InB_2 yielded HfBO [84]. These contrasting transformations are discussed in Sections 4.1, 4.2.1 and 5.9.

A defining structural feature of typical orthorhombic MAB phases is the presence of B atoms situated at the centers of trigonal prisms formed by six surrounding transition metal (M) atoms. By sharing the rectangular faces of these BM_6 prisms, adjacent B atoms form covalent zigzag chains or networks. MoAlB has B–B distances of about 1.81 Å (Table 1) [1,34,69]. While the majority of experimentally synthesized MAB phases belong to the orthorhombic or tetragonal crystal systems, hexagonal MAB phases (*h*-MAB) such as Ti_2InB_2 (space group $P\bar{6}m2$) have also been recently discovered, further expanding the structural diversity of this material family [21,84].

Table 1 and Fig. 4 compare the calculated response of individual interatomic distances to hydrostatic pressure in representative Cr–Al–B and Mo–Al–B structures [61,69]. Here, the positive bond-stiffness parameter k is the negative reciprocal of the initial pressure derivative of the normalized distance d/d_0 , evaluated at zero pressure. It measures resistance to bond-length compression within the crystal; it is distinct from a macroscopic elastic modulus, a shear barrier, or a bond dissociation energy.

In the Cr–Al–B entries, k ranges from 434 GPa for Al–Al in hypothetical CrAlB to 1149 GPa for an edge Cr–B interaction in Cr_2AlB_2 . B–B values span 961–1099 GPa. The edge Cr–B values in Cr_2AlB_2 , Cr_3AlB_4 , and Cr_4AlB_6 span 813–1149 GPa, while interior values include 724 and 934 GPa in Cr_3AlB_4 and 813–952 GPa in Cr_4AlB_6 (Table 1) [61]. The overlapping ranges indicate site-dependent

compressibility without a monotonic trend with slab thickness.

The Cr–Al values are 649, 617, 610, and 599 GPa in CrAlB, Cr₂AlB₂, Cr₃AlB₄, and Cr₄AlB₆, respectively. For the three single-Al-layer structures, the reported Al–B values are 571–595 GPa; hypothetical double-Al-layer CrAlB has an Al–Al value of 434 GPa [61]. The Al–B entries describe the atom pairs analyzed in that study, which assigned relatively weak metallic character to B–Al and Cr–Al interactions. Comparison with Cr–C in Cr₂AlC is a comparison of different structures and interactions, rather than substitution of C by Al within the same bond.

For MoAlB, the corresponding B–B and selected Mo–B values are 1205 and 1135 GPa, whereas Mo–Al, Al–B, and Al–Al give 731, 717, and 526 GPa, respectively (Table 1) [69]. The normalized compression curves in Fig. 4(e) illustrate this contrast within the double-Al-layer structure. The electronic-density maps in Fig. 4(f–g) provide complementary information about charge redistribution in the specific Cr₂AlB₂ and MoAlB models; their interpretation is developed in Section 4.2.1.

The common trend in these selected calculations is a relatively stiff boride framework coupled to more compressible Al-related regions, with the detailed ordering depending on structure and atomic site. Hydrostatic bond compression alone does not identify the operative slip plane, crack path, or selective-etching reaction. Those connections require electronic and deformation calculations (Sections 4.2.1–4.2.2) and material-specific experimental evidence (Sections 5.9 and 6.1).

Stoichiometry, symmetry, boron-network topology, A-layer stacking and chemical ordering jointly describe the structural diversity of MAB phases. In

conventional Al-containing members, compliant M–A and, where present, A–A regions connect this architecture to deformation and selective chemistry. The related 211-type MAX borides and other subfamilies require their own composition-specific bonding descriptions.

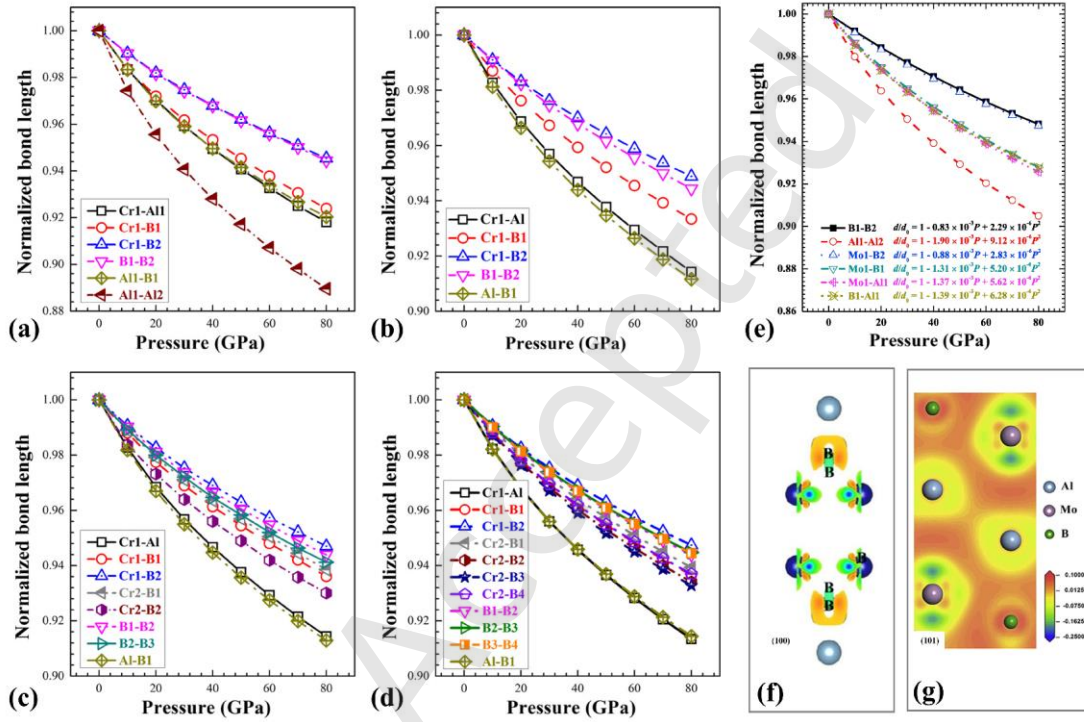


Fig. 4. DFT-calculated bonding hierarchy in representative MAB phases. (a–d) Normalized bond lengths (d/d_0) as a function of hydrostatic pressure for (a) CrAlB, (b) Cr₂AlB₂, (c) Cr₃AlB₄, and (d) Cr₄AlB₆ [61]. (e) Normalized bond lengths versus pressure for MoAlB with second-order polynomial fits [69]. (f) Valence-electron density difference map ($\Delta\rho$) for Cr₂AlB₂ on the (100) plane (isosurface = 0.01 e/Å³) [61]. (g) Valence-electron density difference map for MoAlB on the (101) plane [69]. Adapted with permission from Ref. [61] for (a – d,f), © The American Ceramic Society 2019; Ref. [69] for (e,g), © Acta Materialia Inc. 2017, published by Elsevier Ltd.

Table 1. Bond lengths (d , Å) and bond stiffness (k , GPa) for all symmetry-inequivalent bond types in the Cr–Al–B and Mo–Al–B MAB phase series, together with related binary borides (CrB, CrB₂, MoB) and MAX phases (Cr₂AlC, Mo₂AlC) as reference compounds. Experimental bond lengths are marked "Exp." in the Ref. column; other unmarked entries are calculated. The bond-type labels M1 and M2 denote transition-metal sites at the slab edge and interior, respectively; M–C denotes the metal–carbon bond in MAX-phase reference compounds.

Compound	Parameter	M1–Al1	M1–B1	M1–B2	M–C	M2–B1	M2–B2	M2–B3	M2–B4	B1–B2	B2–B3	B3–B4	Al1–B1	Al1–Al2	Ref.
Cr ₂ AlB ₂	d	2.6551	2.1784	2.1936	–	–	–	–	–	1.768	–	–	2.288	–	[61]
	d	2.6443	2.2014	2.1876	–	–	–	–	–	1.7616	–	–	2.2765	–	Exp. [1]
	k	617	813	1149	–	–	–	–	–	1099	–	–	571	–	[61]
Cr ₃ AlB ₄	d	2.663	2.1747	2.1333	–	2.3377	2.274	–	–	1.7475	1.753	–	2.2549	–	[61]
	d	2.6487	2.19	2.144	–	2.322	2.2702	–	–	1.7358	1.7383	–	2.2444	–	Exp. [1]
	k	610	862	1075	–	934	724	–	–	1031	961	–	581	–	[61]
Cr ₄ AlB ₆	d	2.6715	2.174	2.1239	–	2.33	2.2641	2.2733	2.2902	1.7524	1.7475	1.713	2.2449	–	[61]
	d	2.6621	2.195	2.146	–	2.329	2.2772	2.285	2.277	1.7384	1.7387	1.707	2.2345	–	Exp. [1]
	k	599	869	1099	–	952	840	813	877	1031	1053	1031	595	–	[61]
CrAlB	d	2.6012	2.2431	2.218	–	–	–	–	–	1.744	–	–	2.222	2.681	[61]
	k	649	694	1075	–	–	–	–	–	1063	–	–	641	434	[61]
Cr ₂ AlC	d	2.6652	–	–	1.9606	–	–	–	–	–	–	–	–	–	[86]
	k	495	–	–	1020	–	–	–	–	–	–	–	–	–	[87]
CrB	d	–	2.1712	2.212	–	–	–	–	–	1.7841	–	–	–	–	[61]
	d	–	2.182	2.251	–	–	–	–	–	1.778	–	–	–	–	Exp. [88]
	d	–	2.158	2.2	–	–	–	–	–	1.722	–	–	–	–	[89]
	k	–	917	1123	–	–	–	–	–	1149	–	–	–	–	[61]
CrB ₂	d	–	2.275	2.275	–	–	–	–	–	1.7274	–	–	–	–	[61]
	d	–	2.258	2.258	–	–	–	–	–	1.717	–	–	–	–	Compiled [61,90]
	d	–	2.284	2.284	–	–	–	–	–	1.703	–	–	–	–	[91]

Compound	Parameter	M1–Al1	M1–B1	M1–B2	M–C	M2–B1	M2–B2	M2–B3	M2–B4	B1–B2	B2–B3	B3–B4	Al1–B1	Al1–Al2	Ref.
MoAlB	<i>k</i>	–	819	819	–	–	–	–	–	1205	–	–	–	–	[61]
	<i>d</i>	2.7117	2.3735	2.3541	–	–	–	–	–	1.8085	–	–	2.3209	2.6669	[69]
	<i>d</i>	2.6933	2.346	2.3562	–	–	–	–	–	1.8107	–	–	2.2928	2.6472	Exp. [1]
Mo ₂ AlC	<i>k</i>	731	764	1135	–	–	–	–	–	1205	–	–	717	526	[69]
	<i>d</i>	2.7903	–	–	2.117	–	–	–	–	–	–	–	–	–	[87]
	<i>k</i>	515	–	–	1111	–	–	–	–	–	–	–	–	–	[87]
MoB	<i>d</i>	–	2.3237	2.348	–	–	–	–	–	1.8423	–	–	–	–	[69]
	<i>d</i>	–	2.3132	2.3466	–	–	–	–	–	1.8436	–	–	–	–	Exp. [1]
	<i>k</i>	–	1031	1170	–	–	–	–	–	1060	–	–	–	–	[69]
Al	<i>d</i>	–	–	–	–	–	–	–	–	–	–	–	–	2.864	[69]

“Compiled” identifies the CrB₂ bond lengths reproduced from Ref. [61], which cites Ref. [90]; this citation does not establish an experimental source.

The structural and bonding diversity described above provides the basis for comparing MAB and MAX phases. Table 2 consolidates representative evidence from the bond-stiffness calculations in Table 1, the calculated-property, synthesis and experimental-property data in Tables 3–7, and the exfoliation and irradiation discussions in Sections 5.9 and 6.5. The comparison identifies composition-specific opportunities, including hard layered borides, magnetocaloric Fe₂AlB₂, and functional two-dimensional derivatives, alongside limitations in mechanical-data comparability, low-temperature amorphization resistance, and the maturity of exfoliation routes. Reported differences in cracking or environmental stability are interpreted within the tested materials and conditions.

Table 2. Comparative overview of structural, bonding, and property trends: representative MAB phases and MAX phases.

Attribute	MAB phases and related borides within this review	MAX-phase comparators	Evidence and references
Crystal symmetry	Orthorhombic, tetragonal, hexagonal, and trigonal structures; examples include Cmc ₂ m, Cmmm, Immm, I4/mcm, P6 ₃ m2, and R3m. Included 211 MAX borides have P6 ₃ /mmc symmetry.	Conventional MAX structures are hexagonal, typically P6 ₃ /mmc; chemical ordering can lower the symmetry.	Section 3.2; [1,3,20–24,60]
Formula and scope	(MB) _{2x} Al _y (MB ₂) _z has partial coverage; stoichiometry, symmetry, and chemical ordering are separate descriptors.	M _{n+1} AX _n ; conventionally X = C and/or N. Reported X = B compounds create the 211 overlap discussed here.	Section 3.1; [3,22–24,60]
Framework bonding	DFT bond stiffness $k(\text{B–B}) = 961\text{--}1205$ GPa in the listed Cr–Al–B phases and MoAlB. Boron forms composition-dependent chains or networks.	DFT $k(\text{M–C}) = 1020$ GPa in Cr ₂ AlC and 1111 GPa in Mo ₂ AlC. These are selected framework-bond comparisons.	Table 1; [61,69,87]
M–A bond stiffness	DFT $k(\text{M–Al}) = 599\text{--}731$ GPa in the listed Cr–Al–B phases and MoAlB; lower than their stiffest framework bonds.	DFT $k(\text{M–Al}) = 495$ and 515 GPa in Cr ₂ AlC and Mo ₂ AlC, respectively; these values are lower than the MAB values listed here.	Table 1; [61,69,87]
A–A bonding	DFT $k(\text{Al–Al}) = 434$ GPa for CrAlB and 526 GPa for MoAlB, both with double Al layers.	Conventional single-A-layer MAX structures have no equivalent interplane Al–Al pair for this comparison.	Table 1; [61,69,87]
Vickers hardness (GPa)	At 1 N, single crystals: Cr ₂ AlB ₂ , 6–7; Cr ₃ AlB ₄ , 15.0–19.1; WAlB, 21.7. Bulk examples: MoAlB, 10.6; Fe ₂ AlB ₂ , 10.9. See Table 6 for loads and specimen states.	Ti ₃ AlC ₂ : 2.5–4.7, depending on indentation load, for the fully dense polycrystalline material in [92].	Table 6; [1,2,4,92]
Damage tolerance D_t (m^{1/2})	Selected calculated proxies in Table 6 range from 0.250 to 0.565 m ^{1/2} . Several estimates use representative E from another reference (Table 6, note a).	Selected reference values compiled in Table 6 include Ti ₃ AlC ₂ = 1.948 and Ti ₃ SiC ₂ = 1.244 m ^{1/2} . Input-source and matching details are given in Table 6.	Table 6 and note a; [93]

Attribute	MAB phases and related borides within this review	MAX-phase comparators	Evidence and references
Fracture and deformation	Fe ₂ AlB ₂ shows stepwise post-peak failure and grain pullout; delamination and crack deflection occur in selected layered borides. Responses depend on composition and microstructure.	Layered MAX ceramics can dissipate energy through delamination, interlocking grains, and crack deflection; loading and temperature affect the failure mode.	Section 6.1; [4,92–94]
Machinability	Partial machining with carbide tools is demonstrated for Mn ₂ AlB ₂ .	Conventional machining is demonstrated for representative MAX ceramics, including Ti ₃ AlC ₂ .	Section 6.1; [92,95]
Thermal expansion (10⁻⁶ K⁻¹)	Compiled values: MoAlB, 9.5–10.1; Fe ₂ AlB ₂ , 10.3–13.5; Mn ₂ AlB ₂ , 18.6; included 211 borides Zr ₂ SB and Nb ₂ SB, 7.64 and 7.1. Averaging intervals matter.	Ti ₃ AlC ₂ : approximately 9.0 (100–1000 °C; mean linear expansion from neutron diffraction on the Ti ₃ AlC ₂ constituent of a multiphase specimen, summarized in [96]).	Table 7; [2,92,95–101]
Electrical conductivity (10⁶ S·m⁻¹)	Reported bulk values include MoAlB, 2.04–2.91; Fe ₂ AlB ₂ , 0.374–0.617; Mn ₂ AlB ₂ , 0.19–0.20.	Ti ₃ AlC ₂ : 3.48 at room temperature for the fully dense material in [92].	Table 7; [2,4,92,95,98,99,102,103]
Thermal conductivity (W·m⁻¹·K⁻¹)	Reported bulk values include MoAlB, 29.21–37.56; Fe ₂ AlB ₂ , 7.47–7.5; WAlB, 10.38. Density, composition, and temperature affect transport.	Ti ₃ AlC ₂ -based specimen: approximately 17 near 300 K (96.65 vol.% Ti ₃ AlC ₂ and 3.35 vol.% TiC; stationary heat-flow measurement) [104]. Total thermal conductivity.	Table 7; [2,98,99,102,103,105]; [104]
Oxidation and high-temperature stability	MoAlB can form a protective Al ₂ O ₃ scale; volatilization of Mo and B oxides affects scale development. The behavior of powders and dense bulk material must be distinguished.	Al-containing MAX phases can also form protective Al ₂ O ₃ . Other oxides, scale adherence, temperature, and exposure history determine protection.	Section 6.3; [2,7,92,106–108]
Oxidation-induced crack healing	MoAlB: Al ₂ O ₃ fills cracks; approximately 96% flexural-strength recovery after 1200 °C for 4 h in air is reported in Section 6.3.2.	Ti ₂ AlC: repeated healing by Al ₂ O ₃ with some TiO ₂ . Cr ₂ AlC: oxide filling and strength recovery investigated at 1100 °C.	Section 6.3.2; [7,107,108]
Radiation response	Low-temperature amorphization can occur in MoAlB and Fe ₂ AlB ₂ . Fe ₂ AlB ₂ showed no surface cracking in the cited He-irradiation tests from room temperature to 700 °C.	Selected Ti ₃ SiC ₂ and Ti ₂ AlC tests show greater amorphization resistance but irradiation-induced cracking. Ion species, energy, dose, and temperature control comparisons.	Section 6.5; [9,109–111]

Attribute	MAB phases and related borides within this review	MAX-phase comparators	Evidence and references
2D derivative synthesis	Selective removal of A and sometimes a second metal can yield MBenes. HCl, hydrothermal alkali, and molten-salt routes are demonstrated; incomplete etching and reconstruction must be distinguished from isolated 2D products.	Selective A removal yields MXenes. Fluoride-containing wet etchants are common, but fluorine-free routes also exist; fluorine-free synthesis is not exclusive to MBenes.	Section 5.9; [10,11,29,36,45,60,112]
2D derivative stability	Stability depends on composition, surface terminations, pH, and electrode potential. Boridene stability calculations and MoBT _x sensor tests probe different observables.	Oxidation of MXenes depends on composition and storage or operating conditions. Direct degradation measurements are needed to assess chemical stability.	Sections 4.3 and 6.6; [17,56]
Functional opportunities	Bulk: Fe ₂ AlB ₂ magnetocaloric response. Derivatives: storage, catalysis, and sensing. Pt–MoAl _{1-x} B requires 18 mV (acid) or 32 mV (alkali) at 10 mA·cm ⁻² for HER; these are Pt single-atom catalyst results.	Bulk MAX phases combine electrical conduction and high-temperature mechanical performance; MXenes support storage, shielding, and other surface-dependent functions. Device metrics require matched configurations.	Sections 6.2 and 6.6; [13,27,28,56,60,92,99,102]

[†] Bond stiffness k is a calculated pressure-response metric, not a measured elastic modulus; Table 1 includes both experimentally established and predicted reference structures. Numerical entries are representative literature results, not universal family ranges. The shared 211 MAX-boride subset is included in the MAB scope column; MAX property comparators refer to the explicitly named carbide phases.

^a $D_t = (K_{IC}/\sigma_b)(E/H)$, with units m^{1/2} [93]. E and H must use consistent units. Cross-source E estimates in Table 6 limit quantitative comparisons and should not be interpreted as sample-matched measurements.

^b Irradiation comparisons depend on ion species, energy, dose, temperature and damage criterion (Section 6.5).

^c The 2D entries distinguish material stability from device response and identify catalyst composition where quantitative HER data are quoted. See Section 6.6 for individual experimental and theoretical studies.

4. Prediction on the Stability and Intrinsic Properties of MAB Phases

4.1 Computational Prediction of Materials Stability

The compositional space of MAB phases is vast, defined by the choices of transition metals (M), A-group elements (A), stoichiometric ratios, and, in quaternary systems, the introduction of a second M or A element. Computational prediction therefore serves as an indispensable guide for identifying promising synthetic targets prior to labor-intensive experimental trials. Over the past decade, density functional theory (DFT)-based methodologies have evolved from isolated case studies toward systematic high-throughput screening paradigms, yielding a substantially expanded map of predicted stable and metastable MAB phases, several of which have subsequently been realized experimentally.

4.1.1 Thermodynamic Stability: Formation Energy and Convex Hull Construction

Formation energy relative to the constituent elements provides an initial energetic screen [62,65]. In Eq. (1), the compound energy is taken per chemical formula and the elemental reference energies per atom; comparison with values reported in eV or meV per atom requires division by the total number of atoms in that formula:

$$\Delta E_f(M_xA_yB_z) = E(M_xA_yB_z) - xE(M) - yE(A) - zE(B) \quad (1)$$

A negative ΔE_f indicates that the compound is energetically favorable relative to decomposition into the pure elements. However, as convincingly demonstrated by Carlsson et al. in their systematic survey of 210 MAB-phase compositions across both

orthorhombic ($Cmmm/Cmcm$) and hexagonal ($P\bar{6}m2$) symmetries, formation energy alone is a rather poor stability discriminator. Among the 210 compositions considered, 208 exhibited $\Delta E_f < 0$, yet only 10 were predicted to be thermodynamically stable against the competing phases included in that study [65].

Competition with other compounds is assessed by minimizing the energy of phase combinations at the target composition [65]. In the signed convention used for ΔH_{cp} here, the candidate is compared with a competing-phase set that excludes the candidate itself: $\Delta H_{cp} < 0$ means that it lowers the competing-phase hull, while $\Delta H_{cp} = 0$ indicates degeneracy. After including the candidate and rebuilding the hull, the usual energy above the hull, E_{hull} , is non-negative and equals zero for a hull phase. These classifications depend on the competing phases and computational assumptions; positive-energy screening windows are study-specific.

The competing-phase approach predates the later broad screening surveys. Bai et al. applied a composition-constrained Simplex minimization to $CrAlB$, Cr_2AlB_2 , Cr_3AlB_4 and Cr_4AlB_6 in their 2019 study [61], following the competing-phase methodology previously developed for MAX phases. Its phase-specific stability and bond-stiffness analyses provide an early reference point for the subsequent MAB surveys [62,65].

Qi et al. subsequently screened Al- and Si-containing borides across six structural prototypes by combining composition-constrained optimization over known competing phases with phonon calculations [113]. Of the 43 compositions that passed the energetic test, 14 exhibited imaginary phonon modes, leaving 29 candidates that

satisfied both criteria: 19 Al-containing and 10 Si-containing phases, including 15 members already identified experimentally at the time. Eight of the ten Si-containing candidates adopted the 512 structure; the other two were Cr_2SiB_2 and Cr_4SiB_4 . These results illustrate how the A element changes the favored structural population, while separating energetic stability from lattice-dynamical stability. The authors noted limited competing-phase information for Tc-containing systems, and the remaining predictions still require experimental assessment.

Liu et al. screened 58 MAB-phase structures and retained 23 with favorable elemental formation energies and reported phonon and elastic stability: nine 222-type $\text{M}_2\text{Al}_2\text{B}_2$ and fourteen 212-type M_2AlB_2 compounds [62]. This energetic criterion should be distinguished from a competing-phase convex-hull assessment. Carlsson et al. reported 10 hull-stable compositions, including the predicted Zr_2InB_2 , Hf_2InB_2 and Mo_4AlB_4 , and 23 additional near-stable compositions [65]. Their experimentally known Cr_3AlB_4 and Cr_4AlB_6 had $\Delta H_{\text{cp}} = +4$ and $+17$ meV/atom, respectively; the latter supplied a study-specific metastability reference, not a general synthesis threshold.

Koutná et al. considered 600 models across 60 M–A–B chemical systems and 10 structure prototypes, retaining 317 after energetic preselection and elastic and phonon checks [63]. The authors explicitly excluded competing non-MAB binary and ternary phases, so these candidates are not established equilibrium phases of complete ternary diagrams. In a separate 855-compound study, Xue et al. retained 336 candidates using a near-hull screening window of 200 meV/atom together with phonon and elastic

checks [114]. The counts therefore describe different model spaces and acceptance criteria, rather than directly comparable numbers of equilibrium-stable or experimentally realized phases.

Alongside these high-throughput efforts, compound-focused DFT studies have examined candidate stoichiometries using different energetic references. Tang et al. used CASTEP with ultrasoft pseudopotentials and GGA-PBE to study Ti_2AlB_2 , Ti_3AlB_4 and Ti_4AlB_6 in the 212–314–416 series [115]. Their elemental-reference formation energies and the reaction enthalpies of selected AlB_2 -based precursor routes are negative, whereas the supplementary comparison against TiAl and TiB_2 gives positive competing-phase enthalpies. The reported phonon spectra support harmonic dynamical stability, while the positive competing-phase enthalpies identify these compositions as metastable synthesis candidates. Lu et al. reported elemental-reference formation enthalpies of -0.516 , -0.490 , and -0.336 eV/atom for Cr_4AlB_4 , Mo_4AlB_4 , and W_4AlB_4 , respectively, together with separate cohesive-energy calculations [76]. These quantities do not by themselves establish stability against every competing compound. Dai et al. provided an in-depth theoretical investigation of the newly discovered Cr_4AlB_4 phase, revealing through energy evaluations that Cr_4AlB_4 is thermodynamically favored under Al-lean synthesis conditions and may further transform to Cr_2AlB_2 in Al-rich environments. This insight directly links computational stability predictions with experimental synthesis pathway design and rationalizes why certain MAB phases coexist in experimentally prepared samples [116].

The foundational theoretical work that established stability trends across the 3d transition metal series was conducted by Kádas et al., who combined DFT calculations with experimental characterization to examine the phase stability of the M_2AlB_2 series ($M = Cr, Mn, Fe, Co, Ni$). Their results demonstrated that Cr_2AlB_2 , Mn_2AlB_2 , and Fe_2AlB_2 are thermodynamically stable phases, while Co_2AlB_2 and Ni_2AlB_2 are metastable. Their COHP analysis attributed the decrease in M–M bond strength across the series to increasing occupation of antibonding states [117].

A-site substitution also changes structural preferences. Within the Al-, Ga- and In-containing compositions examined by Carlsson et al., orthorhombic structures were generally favored for Al, whereas many Ga- and In-based candidates preferred hexagonal symmetry [65]. This trend complements the experimental Ti_2InB_2 example [21] and the broader prototype comparisons in Ref. [63].

Extending the comparison to S-containing MAX compounds, Lu et al. screened 138 carbide and boride candidates using composition-constrained competing-phase minimization and reported phonon checks [96]. Their retained set comprised 15 carbides and three related 211-type MAX borides, Zr_2SB , Nb_2SB and Hf_2SB . Nine candidates had a competing-phase energy difference at or below zero; nine further candidates were admitted within the study's positive window of up to 36 meV/atom, including Nb_2SB at +4 meV/atom. This 18-member set therefore combines energetically favored and near-stable candidates under the assessed phase competition. The positive threshold is a study-specific screening choice, rather than a universal criterion for synthesis; the three borides were already experimentally known.

Turning to quaternary systems, stability predictions become considerably more complex owing to the combinatorial explosion of possible M-site and A-site configurations. The MAB phase community has developed two conceptually distinct strategies to address this challenge, which are discussed in **Section 4.1.4** after the treatment of dynamic and mechanical stability criteria.

4.1.2 Dynamic Stability: Phonon Dispersion Calculations

A favorable energy relative to competing phases does not replace a test of lattice vibrations. Harmonic phonon calculations examine the response to atomic displacements about a relaxed structure [118]. The absence of significant imaginary modes supports local dynamical stability within the sampled wave vectors and numerical convergence; the translational acoustic modes approach zero at the zone center. It does not establish finite-temperature stability or a synthetic pathway, and homogeneous-strain stability is assessed separately in Section 4.1.3.

Phonon calculations support the local stability assignments for the 23 candidates in Ref. [62] and the Cr_4AlB_4 , Mo_4AlB_4 and W_4AlB_4 structures in Ref. [76]. They also help distinguish hexagonal candidates in the survey by Liu et al. [119]. Screening order varies among studies: Koutná et al. applied phonon checks to mechanically stable candidates after energetic preselection [63], whereas Ref. [65] focuses on competing-phase energetics. Screening criteria vary among these studies [114].

Phonon spectra computed for stability verification simultaneously provide the foundation for thermodynamic property predictions: within the quasi-harmonic approximation (QHA), the volume-dependent phonon density of states yields the

vibrational contributions to the Helmholtz free energy, from which the thermal expansion coefficient, heat capacity, Grüneisen parameter, and Debye temperature can be obtained [120,121]. Higher-order force constant calculations further enable the prediction of lattice thermal conductivity via the phonon Boltzmann transport equation. These property predictions, which build upon the phonon stability verification discussed here, are treated in detail in Section 4.2.

4.1.3 Mechanical Stability: Elastic Constants and the Born Criteria

For an unstressed crystal, mechanical stability against infinitesimal homogeneous strain requires a positive-definite elastic matrix C_{ij} [118,122]. For orthorhombic structures, this condition gives the following inequalities:

$$C_{11}, C_{22}, C_{33}, C_{44}, C_{55}, C_{66} > 0, \quad (2)$$

$$C_{11}C_{22} - C_{12}^2 > 0, \quad C_{11}C_{33} - C_{13}^2 > 0, \quad C_{22}C_{33} - C_{23}^2 > 0, \quad (3)$$

$$C_{11}C_{22}C_{33} + 2C_{12}C_{13}C_{23} - C_{11}C_{23}^2 - C_{22}C_{13}^2 - C_{33}C_{12}^2 > 0. \quad (4)$$

Other crystal symmetries require their corresponding elastic conditions; under finite external stress, the relevant stress-corrected stability tensor must be used [122].

The phonon and elastic tests both probe local stability and are physically related, but a finite phonon calculation is not a substitute for verifying the response to homogeneous strain. Likewise, a favorable chemical energy does not verify elastic stability. For example, mechanically stable Co_2AlB_2 and Ni_2AlB_2 were assessed as metastable against competing phases [117]. Elastic checks complement energetic screening [62,63,114]. These elastic constants also determine the moduli and anisotropy descriptors in Section 4.2.2.

4.1.4 Solid Solutions and the Role of Configurational Entropy

Solid solution formation is an effective means of continuously tuning material properties across compositional space, including elastic stiffness, magnetic behavior, and thermal expansion. However, the computational prediction of solid solution stability introduces an additional layer of complexity beyond that required for ordered stoichiometric compounds. The configurational entropy contribution to the Gibbs free energy, $\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{config}}$, must be quantitatively evaluated at experimentally relevant synthesis temperatures, since many solid solutions that appear unstable or metastable at 0 K become thermodynamically favored when the entropic stabilization at high temperature is properly accounted for.

Hanner et al. provided a prototypical demonstration of this approach by combining the Special Quasirandom Structure (SQS) method with finite-temperature Gibbs free energy calculations. They theoretically predicted the formation ranges of $(\text{Mn}_{1-x}\text{Cr}_x)_2\text{AlB}_2$ and $(\text{Mn}_{1-x}\text{Cr}_x)_3\text{AlB}_4$ solid solutions, with calculations indicating full mutual solubility across the entire composition range at synthesis-relevant temperatures. This result was subsequently validated by the successful experimental synthesis of the predicted solid solutions, achieving a close and productive integration of computational prediction and experimental verification [123].

The quantitative treatment of configurational entropy has proven essential for reliable stability predictions of disordered M-site solid solutions in quaternary MAB-phase systems. In the original *i*-MAB study, Dahlqvist et al. [20] evaluated the thermodynamic stability of 182 unique M'/M'' combinations in Al-containing

$M'_{2-x}M''_xAlB_2$ compositions by comparing ΔH_{cp} for chemically ordered *i*-MAB candidates with ΔG_{cp} for disordered *Cmmm* and $P\bar{6}m2$ solid-solution models. The configurational entropy was treated using an ideal-solution approximation, $\Delta S_{config} = -2k_B[y \ln y + (1-y) \ln (1-y)]$, where y denotes the fraction of M'' on the mixed M sublattice. At a representative synthesis temperature of 2000 K, their calculations identified 15 stable chemically ordered *i*-MAB phases and 16 stable disordered solid-solution MAB phases, with an additional 13 ordered and 17 disordered phases falling within a metastable window of $0 < \Delta H_{cp}$ or $\Delta G_{cp} < +25$ meV/atom [20]. A subsequent broader survey over 1092 M_2AB_2 -based compositions with $A = Al, Ga, In, Si, Ge,$ and Sn further showed that experimentally known *Cmmm* solid-solution phases are unstable at 0 K but become stable at 2000 K when configurational entropy is included, underscoring the importance of finite-temperature thermodynamics [19]. The synthesis and structural verification of the predicted *i*-MAB phases $Mo_{4/3}Y_{2/3}AlB_2$ and $Mo_{4/3}Sc_{2/3}AlB_2$ provided direct experimental validation of this *i*-MAB stability-prediction framework [20].

Extending this methodology to *o*-MAB (out-of-plane chemically ordered) phases and T2-type solid solutions, Dahlqvist et al. screened 910 unique quaternary compositions across $A = Al, Si, P, Ga,$ and Ge , evaluating both the formation enthalpy of ordered structures and the Gibbs free energy of disordered solid solutions at 2000 K. Their predictions yielded 35 chemically ordered *o*-MAB phases and 121 stable solid solutions, dramatically expanding the known compositional space of quaternary metal borides [82]. The *o*-MAB phases Ti_4MoSiB_2 , Mo_4CrSiB_2 , W_4CrSiB_2 , and Nb_4CrSiB_2

were subsequently synthesized and structurally characterized, confirming the predictive capability of the entropically corrected stability model [14,81,124]. In a parallel effort, Dai et al. [42] explored *o*-MAB phases adopting the Cr_3AlB_4 -type structure, predicting that $\text{M}_2\text{M}'\text{AlB}_4$ phases with $\text{M} = \text{Mn, Fe, Co}$ and $\text{M}' = \text{Cr, Mo, W}$ exhibit a strong thermodynamic driving force toward chemical ordering on the transition-metal sublattice. The ordering tendency was attributed mainly to differences in Al–transition-metal bond strengths [42].

4.1.5 Advanced Methodologies and Outlook

Cluster expansion combined with crystal structure prediction extends the search beyond a fixed list of prototypes. For the $(\text{Mo}_x\text{Sc}_{1-x})_2\text{AlB}_2$ system, Carlsson et al. recovered the known *i*-MAB composition $\text{Mo}_{4/3}\text{Sc}_{2/3}\text{AlB}_2$ and predicted $\text{Sc}_4\text{Mo}_2\text{Al}_3\text{B}_6$ [125]. The approach explores chemical ordering and alternative structures together; extending it to additional elements requires suitable training structures and renewed energetic validation.

Rossignol et al. used machine-learning interatomic potentials to preselect structures before DFT convex-hull construction for Cu–Ag–Au and Mo–Ta–W alloys [126]. These are adjacent methodological examples, rather than demonstrated MAB-phase predictions. For quaternary and quinary MAB-phase compositions, the chemical coverage needed to adapt these models to MAB-phase compositional space must include boron environments, relevant competing phases, and independent DFT validation (Section 7.2.2).

Magnetic screening provides a further connection between composition and

predicted function. For seven Fe-, Mn- or Co-containing compositions retained in their survey, Qi et al. calculated finite magnetic moments and estimated ordering temperatures from ferromagnetic–antiferromagnetic energy differences within a mean-field approximation [113]. For Fe_2AlB_2 , the resulting Curie-temperature estimate was 329 K. The estimated ordering temperatures depend on the modeled magnetic configurations.

Magnetic MAB phases represent a promising yet largely unexplored materials family. A high-throughput screening study systematically evaluated their stability and functional properties, predicting 21 stable and 434 metastable (within 100 meV/atom) compounds across various transition metals, beyond just Mn- and Fe-based systems [64]. Functionally, it identified 71 candidates with high magnetocrystalline anisotropy ($>1.0 \text{ MJ/m}^3$) for permanent magnets and 99 with a high magnetic deformation proxy ($>1.5\%$) for magnetocaloric applications. Furthermore, the study established that atomic size factor and valence electron concentration are key design principles for stability in these layered borides, offering direct guidance for synthesizing novel magnetic MAB phases for energy technologies [64].

Chemical competition, local lattice stability and finite-temperature effects provide complementary criteria for screening candidates. Successful predictions in ordered and solid-solution systems provide useful examples [19,20,82], while a feasible route still depends on precursor chemistry, reaction kinetics, chemical potentials and the temperature-dependent phase landscape. This distinction guides the synthesis discussion in Section 5 and the property calculations in Section 4.2.

Table 3. Bulk modulus (B , GPa), shear modulus (G , GPa), and Young's modulus (E , GPa) of MAB phase compounds grouped by structural type, as derived from first-principles DFT calculations.

Crystal type	Chemical formula	Crystal system	Space group	G (GPa)	B (GPa)	E (GPa)	Ref.
222	MoAlB	Orthorhombic	$Cmcm$	137	207	336	[69]
222	MoAlB	Orthorhombic	$Cmcm$	146	213	357	[127]
222	MoAlB	Orthorhombic	$Cmcm$	144	209	351	[128]
222	WAlB	Orthorhombic	$Cmcm$	146	232	362	[127]
222	WAlB	Orthorhombic	$Cmcm$	147	225	362	[128]
222	WAlB	Orthorhombic	$Cmcm$	134	212	333	[129]
212	Fe ₂ AlB ₂	Orthorhombic	$Cmmm$	141	215	348	[130]
212	Fe ₂ AlB ₂	Orthorhombic	$Cmmm$	139	232	347	[117]
212	Mn ₂ AlB ₂	Orthorhombic	$Cmmm$	165	256	407	[117]
212	Cr ₂ AlB ₂	Orthorhombic	$Cmmm$	197	259	472	[117]
212	Cr ₂ AlB ₂	Orthorhombic	$Cmmm$	163	220	392	[131]
212	Cr ₂ AlB ₂	Orthorhombic	$Cmmm$	169	202	397	[132]
h -MAB 212	Mo ₂ GaB ₂	Hexagonal	$P\bar{6}m2$	130	215	326	[133]
h -MAB 212	Mo ₂ GeB ₂	Hexagonal	$P\bar{6}m2$	127	238	323	[133]
212	Cr ₂ SiB ₂	Orthorhombic	$Cmmm$	143	269	365	[63]
314	Cr ₃ AlB ₄	Orthorhombic	$Pmmm$	182	237	440	[131]
314	Cr ₃ AlB ₄	Orthorhombic	$Pmmm$	173	222	412	[132]
414	Cr ₄ AlB ₄	Orthorhombic	$Immm$	199	255	474	[76]
414	Mo ₄ AlB ₄	Orthorhombic	$Immm$	159	262	398	[76]
414	W ₄ AlB ₄	Orthorhombic	$Immm$	166	288	419	[76]
416	Cr ₄ AlB ₆	Orthorhombic	$Cmmm$	179	254	435	[131]

Crystal type	Chemical formula	Crystal system	Space group	G (GPa)	B (GPa)	E (GPa)	Ref.
416	Cr_4AlB_6	Orthorhombic	$Cmmm$	182	234	434	[132]
512 (T2)	Mn_5SiB_2	Tetragonal	$I4/mcm$	137	193	332	[79]
512 (T2)	Fe_5SiB_2	Tetragonal	$I4/mcm$	104	198	266	[79]
512 (T2)	Mo_5SiB_2	Tetragonal	$I4/mcm$	143	279	365	[124]
i -MAB 212	$(\text{Mo}_{2/3}\text{Y}_{1/3})_2\text{AlB}_2$	Trigonal	$R\bar{3}m$	119	174	292	[83]
i -MAB 212	$(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlB}_2$	Trigonal	$R\bar{3}m$	122	183	299	[83]
i -MAB 212	$\text{Cr}_{4/3}\text{Sc}_{2/3}\text{AlB}_2$	Trigonal	$R\bar{3}m$	138	171	325	[83]
i -MAB 212	$\text{Cr}_{4/3}\text{Y}_{2/3}\text{AlB}_2$	Trigonal	$R\bar{3}m$	131	154	306	[83]
i -MAB 212	$\text{W}_{4/3}\text{Sc}_{2/3}\text{AlB}_2$	Trigonal	$R\bar{3}m$	126	195	310	[83]
i -MAB 212	$\text{W}_{4/3}\text{Y}_{2/3}\text{AlB}_2$	Trigonal	$R\bar{3}m$	124	186	305	[83]
h -MAB 212	Ti_2InB_2	Hexagonal	$P\bar{6}m2$	119	145	280	[134]
h -MAB 212	Ti_2InB_2	Hexagonal	$P\bar{6}m2$	122	147	287	[135]
h -MAB 212	Hf_2InB_2	Hexagonal	$P\bar{6}m2$	114	154	274	[135]
o -MAB 512	$\text{Ti}_4\text{MoSiB}_2$	Tetragonal	$I4/mcm$	103	176	258	[124]
o -MAB 512	Ta_4VSiB_2	Tetragonal	$I4/mcm$	167	252	410	[136]
o -MAB 512	$\text{Ta}_4\text{CrSiB}_2$	Tetragonal	$I4/mcm$	172	261	423	[136]

Crystal type	Chemical formula	Crystal system	Space group	G (GPa)	B (GPa)	E (GPa)	Ref.
h -MAB 212	α -Mo ₂ SiB ₂	Hexagonal	$P\bar{6}m2$	147	253	369	[63]
h -MAB 212	α -W ₂ SiB ₂	Hexagonal	$P\bar{6}m2$	147	273	373	[63]
211	Zr ₂ SB	Hexagonal	$P6_3/mmc$	106	141	254	[137]
211	Zr ₂ SB	Hexagonal	$P6_3/mmc$	102	142	247	[138]
211	Hf ₂ SB	Hexagonal	$P6_3/mmc$	116	154	278	[137]
211	Hf ₂ SB	Hexagonal	$P6_3/mmc$	111	151	267	[22]
211	Nb ₂ SB	Hexagonal	$P6_3/mmc$	124	181	303	[137]
211	Nb ₂ SB	Hexagonal	$P6_3/mmc$	128	186	312	[138]
211	Zr ₂ SeB	Hexagonal	$P6_3/mmc$	106	162	260	[139]
211	Zr ₂ SeB	Hexagonal	$P6_3/mmc$	88	133	216	[24]
211	Hf ₂ SeB	Hexagonal	$P6_3/mmc$	95	144	233	[24]
211	Hf ₂ TeB	Hexagonal	$P6_3/mmc$	73	120	183	[140]
211	Hf ₂ TeB	Hexagonal	$P6_3/mmc$	81	125	199	[141]

4.2 Computational Investigation and Mechanistic Insights into Physicochemical Properties

4.2.1 Electronic Structure and Chemical Bonding

Electronic-structure calculations complement the pressure-response analysis in Section 3.2 by resolving orbital hybridization, charge localization, and pairwise bonding contributions. Finite densities of states at the Fermi level, dominated by transition-metal d states, support metallic electronic behavior in MoAlB and the studied Cr–Al–B compositions [69,131,142]. Li et al. interpreted MoAlB electron-localization-function (ELF) maps as evidence for polar covalent Mo–B

interactions and metallic Mo–Al interactions [143]. Dai et al. additionally described an Al–B covalent–ionic contribution in MoAlB/WAlB [128], whereas Bai et al. described relatively weak metallic B–Al interactions in their Cr–Al–B models [61]. These are material- and analysis-specific assignments, rather than a single A–B bonding character for the entire MAB scope. The local atomic geometry and electronic evidence should accompany such assignments.

Charge-partitioning analyses help assess polarization, but do not independently measure bond strength. Miao et al. reported Bader charges on B of -0.86 , -0.89 , and -0.90 |e| in Ti_2InB_2 , Zr_2InB_2 , and Hf_2InB_2 , compared with -2.03 |e| in the related 211-type MAX boride Hf_2BiB [85]. Their combined ELF, charge, and bonding analyses associate the hexagonal 212/314 examples with covalently connected B layers, while the 211 examples retain substantial M–B covalent contributions as well as stronger charge transfer. The relative covalent and ionic contributions therefore depend on structure and composition; interpretation of charge and bond populations also depends on the atomic pair and computational method.

Crystal orbital Hamilton population (COHP) analysis resolves bonding and antibonding contributions to the electronic band energy. With the convention in which occupied bonding contributions are negative, a more negative integrated COHP (ICOHP) indicates a larger net bonding contribution for a consistently defined atom pair. For the PBE calculations on Cr_4AlB_4 , Mo_4AlB_4 , and W_4AlB_4 , Lu et al. reported B–B values of -4.94 , -4.62 , and -7.73 eV and M–Al values of -1.01 , -1.35 , and -1.42 eV, respectively [76]. Akande and Çakır also used this analysis to compare

covalent interactions in MoAlB, WAlB, Cr₂AlB₂, and Fe₂AlB₂ [144]. These electronic indicators are not interchangeable with the pressure-derived k values in Table 1 or with cleavage energies. Kádas et al. explicitly distinguished ICOHP trends from calculated work-of-separation trends in the 3d M₂AlB₂ series [117]. Khazaei et al. found generally weaker Al-related interactions in their Al-containing survey, but also reported a calculated Ni–Al/Ni–B exception and emphasized the limitations of both ICOHP and force constants [145]. Consequently, relatively weak A-related bonding is a useful composition-specific trend, not an invariant rule for every A element and metal. Static bonding descriptors can guide candidate selection, while successful A-layer removal still depends on reaction conditions and the stability of the resulting product (Section 5.9).

A complementary comparison uses the pressure-derived bond-stiffness ratio $k_{\min}/k_{\max}$, relating the weakest A-related linkage to the strongest bond in the modeled structure. Qi et al. reported ratios of 0.45 for MoAlB and 0.40 for Fe₂AlB₂, compared with 0.68 for Cr₂SiB₂ and Cr₄SiB₄ and 0.75 for Mo₅SiB₂ [113]. The Al-containing phases also showed exceptions to a uniformly low ratio: the four stable Cr–Al–B compositions examined had ratios of 0.53–0.57. The same study compared these calculated ratios with literature fracture toughness measured by the single-edge-notched-beam method for a small selected set of layered ceramics. The resulting correlation suggests a connection between bonding contrast and fracture resistance within that dataset.

The bond-stiffness comparison also distinguishes the related S-containing

211-type MAX borides. Lu et al. reported weakest M–S to strongest M–B stiffness ratios of 0.761, 0.716 and 0.730 for Zr_2SB , Nb_2SB and Hf_2SB , respectively [96]. These values exceed the 0.5 threshold used in their model and support its prediction of relatively brittle behavior, consistent with the indentation cracking previously reported for Zr_2SB and Nb_2SB . The ratio is a bonding descriptor; fracture toughness requires a separate calculation or measurement.

4.2.2 Elastic Properties and Mechanical Anisotropy

Second-order elastic constants of single-crystalline MAB phases are routinely obtained from first-principles stress-strain calculations, from which the polycrystalline bulk modulus (B), shear modulus (G), Young's modulus (E), and Poisson's ratio (ν) can be derived via the Voigt-Reuss-Hill averaging scheme, enabling systematic assessment of stiffness, compressibility, and mechanical anisotropy. The resulting elastic moduli for most typical MAB phases, both experimentally synthesized and theoretically predicted, are comprehensively compiled in Table 3.

As summarized in Table 3, the elastic moduli of MAB phases span a broad range depending on composition and structural type. Within the Cr–Al–B series, Cr_2AlB_2 exhibits shear moduli G of 163–197 GPa, bulk moduli B of 202–259 GPa, and Young's moduli E of 392–472 GPa across multiple independent DFT studies [117,131,132]. Differences in computational settings, including exchange–correlation functional, pseudopotential treatment and implementation, can contribute to this spread. The ranges for the three Cr-based compositions overlap across studies; they do not establish a uniformly increasing modulus sequence. Within each of Refs. [131]

and [132], however, the calculated bulk modulus increases from Cr_2AlB_2 through Cr_3AlB_4 to Cr_4AlB_6 . Specifically, Cr_3AlB_4 shows $G = 173\text{--}182$ GPa, $B = 222\text{--}237$ GPa, and $E = 412\text{--}440$ GPa, whereas Cr_4AlB_6 gives $G = 179\text{--}182$ GPa, $B = 234\text{--}254$ GPa, and $E = 434\text{--}435$ GPa [131,132]. These within-study trends suggest a contribution from the changing M–B slab architecture, while the cross-study ranges require the computational context to be retained. In the 222-type MAB phases, MoAlB displays G of $137\text{--}146$ GPa, B of $207\text{--}213$ GPa, and E of $336\text{--}357$ GPa [69,127,128], and WAlB exhibits G of $134\text{--}147$ GPa, B of $212\text{--}232$ GPa, and E of $333\text{--}362$ GPa [127–129]. Their listed shear and Young's moduli are lower than those of the Cr-based examples, whereas the bulk-modulus ranges overlap. Both composition and layer architecture contribute to this comparison. Among the 211-type MAX borides listed in Table 3, the zero-pressure Nb_2SB results give the highest listed shear and Young's moduli (G of $124\text{--}128$ GPa, B of $181\text{--}186$ GPa, E of $303\text{--}312$ GPa) [137,138], whereas the theoretically predicted 414-type W_4AlB_4 achieves a calculated B of 288 GPa—the largest bulk modulus in Table 3 [76], reflecting the exceptionally rigid W–B framework. Beyond these representative systems, Table 3 further compiles elastic moduli for quaternary *i*-MAB and *o*-MAB phases, hexagonal h-MAB phases and T2-type borides, underscoring the substantial tunability of mechanical properties across the MAB phase family.

The non-spherical Young's modulus surface and non-circular planar projections of MoAlB in Fig. 5(a) show a direction-dependent elastic response [128]. The Young's and shear-modulus projections for Cr_2AlB_2 , Cr_3AlB_4 and Cr_4AlB_6 in Fig. 5(b–d)

likewise resolve material-specific anisotropy [131]. The plotted $E_{\min}/E_{\max}$ values are approximately 320/445 GPa for Cr_2AlB_2 , 378/480 GPa for Cr_3AlB_4 , and 385/506 GPa for Cr_4AlB_6 . In the cited analysis, the largest in-plane Young's modulus anisotropy occurs in the (001) projection for Cr_2AlB_2 and the (100) projection for Cr_3AlB_4 and Cr_4AlB_6 . The direction of the maximum modulus and the plane of greatest anisotropy are distinct descriptors.

The indices in Table 4 describe different aspects of the calculated elastic response. The small bulk anisotropy values ($A_B \leq 1.8\%$ in the listed entries) indicate a small difference between the Voigt and Reuss bulk-modulus bounds; they do not require identical linear compressibility along every crystallographic direction. The shear index A_G is larger than A_B in many entries, including NbAlB (7.19%), TaAlB (6.30%), VAlB (6.10%), WAlB (4.04%), and MoAlB (3.14%), but not in every row: Cr_3AlB_4 has $A_G = 0.5\%$ and $A_B = 0.7\%$, and Cr_4AlB_6 has 0.5% for both (Table 4 [120,146–151]). More specific deformation evidence is provided by the ideal-strength calculations of Dai et al. for MoAlB and WAlB : basal cleavage and shear failure involve the weakly bonded Al–Al bilayers, with layer expansion assisting shear [128]. Section 6.1 compares these predictions with experimental deformation and fracture observations.

A clear structural trend emerges when the anisotropy indices are compared across different MAB-phase series (Table 4). The listed double-Al-layer compounds generally show larger shear and universal anisotropy indices than the single-Al-layer Cr compounds (Table 4). Within the latter group, A^U is 0.179 for Cr_2AlB_2 , 0.065 for

Table 4. Elastic anisotropy indices of MAB phase compounds from first-principles (DFT) calculations: Planar anisotropy factors (A_1 (100), A_2 (010), A_3 (001)), universal anisotropy index (A^U), bulk anisotropy (A_B), and shear anisotropy (A_G).

Material system	Crystal type/ Space group	Sublattice feature	A_1	A_2	A_3	A^U	A_B (%)	A_G (%)
MoAlB [146,147]	222 / <i>Cmcm</i>	2 M–B layers / double Al	1.670	1.330	1.750	0.333	0.480	3.140
NbAlB [147]	222 / <i>Cmcm</i>	2 M–B layers / double Al	1.860	1.660	2.580	0.793	0.770	7.190
TaAlB [148]	222 / <i>Cmcm</i>	2 M–B layers / double Al	2.070	1.750	2.060	0.690	0.800	6.300
VAlB [148]	222 / <i>Cmcm</i>	2 M–B layers / double Al	1.280	2.090	2.210	0.670	0.900	6.100
WAlB [120]	222 / <i>Cmcm</i>	2 M–B layers / double Al	1.840	1.450	1.940	0.420	0.200	4.040
Mo ₃ NbAl ₄ B ₄ [149]	222 / <i>Cmcm</i>	2 M–B layers / double Al	1.813	1.547	2.150	0.516	0.474	4.817
CrAlB [150]	222 / <i>Cmcm</i>	2 M–B layers / double Al	1.566	1.744	2.089	0.254	1.800	2.100
Fe ₂ AlB ₂ [151]	212 / <i>Cmmm</i>	2 M–B layers / single Al	1.075	1.698	1.289	0.216	1.000	1.900
Mn ₂ AlB ₂ [151]	212 / <i>Cmmm</i>	2 M–B layers / single Al	0.807	1.205	1.349	0.121	0.100	1.200
Cr ₂ AlB ₂ [150]	212 / <i>Cmmm</i>	2 M–B layers / single Al	0.794	0.602	0.807	0.179	1.300	1.400
Cr ₃ AlB ₄ [150]	314 / <i>Pmmm</i>	3 M–B layers / single Al	1.125	0.953	1.036	0.065	0.700	0.500
Cr ₄ AlB ₄ [150]	414 / <i>Immm</i>	4 M–B layers / single Al	0.953	0.785	0.938	0.055	0.200	0.500
Cr ₄ AlB ₆ [150]	416 / <i>Cmmm</i>	4 M–B layers / single Al	0.826	0.668	0.959	0.067	0.500	0.500

4.2.3 Thermodynamic and Thermal Transport Properties

First-principles thermal calculations connect vibrational spectra and their volume dependence with measurable heat capacity and thermal expansion. Yin et al. examined 29 Al- and Si-containing MAB compositions using the quasi-harmonic approximation, including electronic excitation and magnetic contributions, over a modeled temperature range extending to 1500 K [121]. For the MoAlB heat-capacity comparison in Fig. 6(a), the authors reported a fitting error below 5% for PBE with electronic excitation relative to Kota et al.'s measurements [121,152]. Those measurements span 4 – 1000 K. Electronic excitation contributes increasingly above room temperature, while magnetic terms become important near a Curie transition. The reported Al/Si trends in heat capacity and expansion (Fig. 6(b)) depend on composition, bonding, normalization and magnetic state; replacement of Al by Si does not itself increase the number of atoms per formula unit. The Debye-temperature trends in Fig. 6(c) provide a stiffness descriptor, while the directional expansion measurements in Ref. [101] provide a separate experimental test of anisotropy.

For S-containing MAX carbides and borides, Lu et al. included phonon and electronic-excitation contributions in a quasi-harmonic free-energy treatment [96]. Their heat-capacity comparisons involved Nb₂SB and the carbide Zr₂SC, whereas thermal-expansion comparisons included Nb₂SB and the carbides Ti₂SC, Zr₂SC and Hf₂SC. For Nb₂SB over 297 – 873 K, the predicted and reported dilatometric average linear expansion coefficients were $(7.847 \text{ and } 7.10) \times 10^{-6} \text{ K}^{-1}$, respectively. The authors discussed porosity and NbB impurities as possible contributors to this

difference.

Thermal-conductivity models must be distinguished from equilibrium thermal-property calculations. Akande et al. compared empirical hardness and lattice-conductivity models using first-principles elastic and vibrational descriptors for MoAlB, WAlB, Cr₂AlB₂ and Ti₂InB₂ [120]. For MoAlB at 300 K, their modified Slack model gives a lattice conductivity of 9.49 W m⁻¹ K⁻¹, compared with an experimentally inferred lattice contribution of 6.33 W m⁻¹ K⁻¹ [120]. These scalar estimates use averaged elastic and vibrational descriptors and should not be assigned to a particular crystal direction. The experimental lattice contribution is obtained by subtracting the electronic contribution, estimated through the Wiedemann–Franz relation, from the measured total conductivity [152]. The modified Slack curves in Fig. 6(d) extend to 1600 K. A separate study reported calculated room-temperature lattice conductivities of 3.2, 6.6 and 41.0 W m⁻¹ K⁻¹ for ZrAlB, NbAlB and MoAlB, respectively [153], attributing the contrast to mode-dependent anharmonicity. These ideal-crystal predictions should be compared at a common composition, direction and temperature, and should not be directly equated with the total experimental conductivities in Table 7. Electronic heat transport, microstructure and the separation of electronic and lattice contributions must also be considered (Section 6.2).

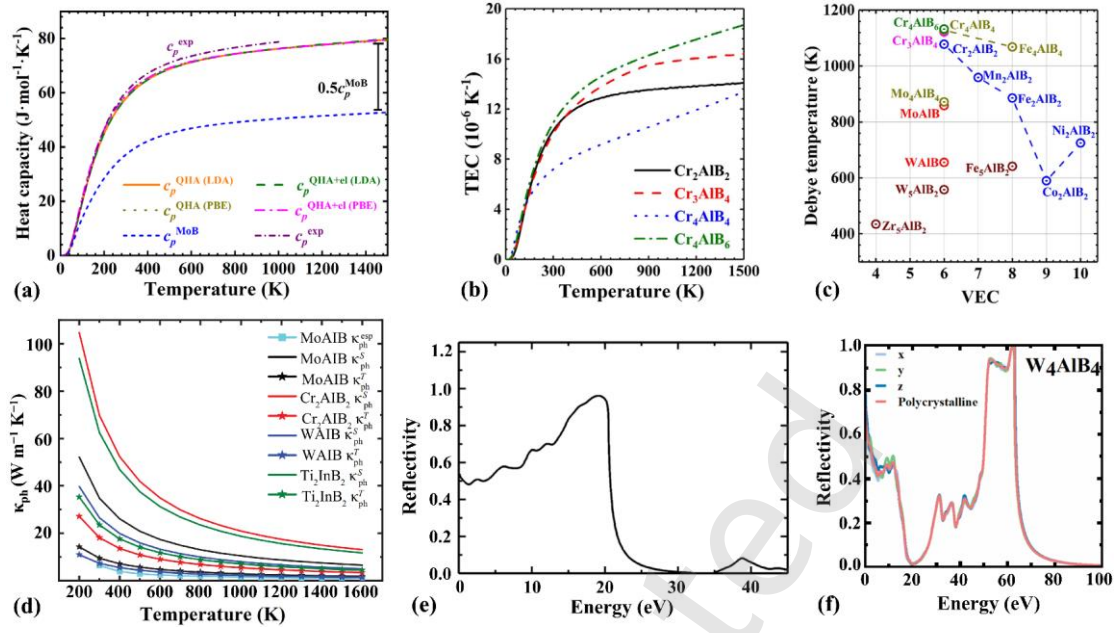


Fig. 6. Calculated thermal and optical observables: (a) MoAlB heat capacity with available measurements, (b) Cr-based thermal expansion and (c) Debye temperature versus electron concentration [121]; (d) modeled lattice conductivity and experimentally inferred MoAlB lattice contribution [120]; (e,f) MoAlB and W₄AlB₄ reflectivity [76,143]. The lattice contribution in (d) is distinct from the experimental total conductivity compiled in Table 7 (Sections 4.2.3 and 6.2). Adapted with permission from Ref. [121] for (a–c), © The American Ceramic Society 2025; Ref. [120] for (d), © American Physical Society 2023. Adapted from Ref. [143] for (e), © The Author(s) 2016, under CC BY 4.0 (<https://creativecommons.org/licenses/by/4.0/>). Adapted with permission from Ref. [76] for (f), © The Author(s) 2024, published by the Royal Society of Chemistry. Ref. [76] is published under CC BY-NC 3.0 (<https://creativecommons.org/licenses/by-nc/3.0/>). Panels have been rearranged.

4.2.4 Optical Properties and Potential Applications

Optical properties are derived from the complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, from which the refractive index, extinction coefficient, absorption coefficient, reflectivity, optical conductivity, and energy-loss function can be extracted [76,143]. Because most investigated MAB phases show metallic electronic structures, intraband transitions can contribute significantly at low photon energies, and a Drude correction is therefore required to describe this contribution. Li et al. [143] incorporated an empirical Drude term with a plasma frequency of 3 eV and a damping parameter of

0.05 eV in their study of MoAlB. As shown in Fig. 6(e), the resulting reflectivity of MoAlB remains high over a broad energy range up to approximately 19 eV and decreases sharply near its plasma frequency of 20.4 eV, above which the material changes from a metallic to a dielectric optical response [143]. Similar metallic optical responses have also been reported for selected 222-type MAB phases: first-principles calculations on ZrAlB, NbAlB, and MoAlB showed reflectivity exceeding 35% in certain frequency bands, suggesting potential applications in optoelectronic and photothermal technologies [153]. A particularly notable result was reported for the M_4AlB_4 series: as shown in Fig. 6(f), W_4AlB_4 exhibits reflectivity exceeding 80% in the extreme ultraviolet (EUV) wavelength range of 19.84–23.6 nm, a feature not observed for Cr_4AlB_4 and Mo_4AlB_4 and attributed to the pronounced optical anisotropy of the W–B electronic framework [76]. This property positions W_4AlB_4 as a candidate material for EUV reflective coatings in EUV lithography and EUV imaging optics [76]. Nevertheless, systematic optical-property studies across the MAB phase family remain limited, and the available results are still dominated by first-principles calculations. Broader composition–structure–optical-property correlations therefore await further computational screening and experimental validation.

4.3 The Role of Computational Simulations in MBene Materials Design

MBene-oriented first-principles work extends beyond the convex-hull and Born-criteria framework used for bulk MAB phases to encompass A-layer exfoliation energetics, surface Pourbaix analysis, and reaction free-energy profiles for

electrocatalytic pathways, covering the property targets surveyed in the representative studies below. For a specified parent and transformation pathway, selective removal or reconstruction can expose boride surfaces whose behavior depends on residual composition, surface chemistry and interfacial energetics [10,11,35]. Calculations on ideal monolayers should be distinguished from the experimentally recovered products identified in Sections 5.9 and 6.6. The following representative studies, selected from recent years, collectively illustrate the breadth of computational contributions across multiple MBene application domains (Fig. 7).

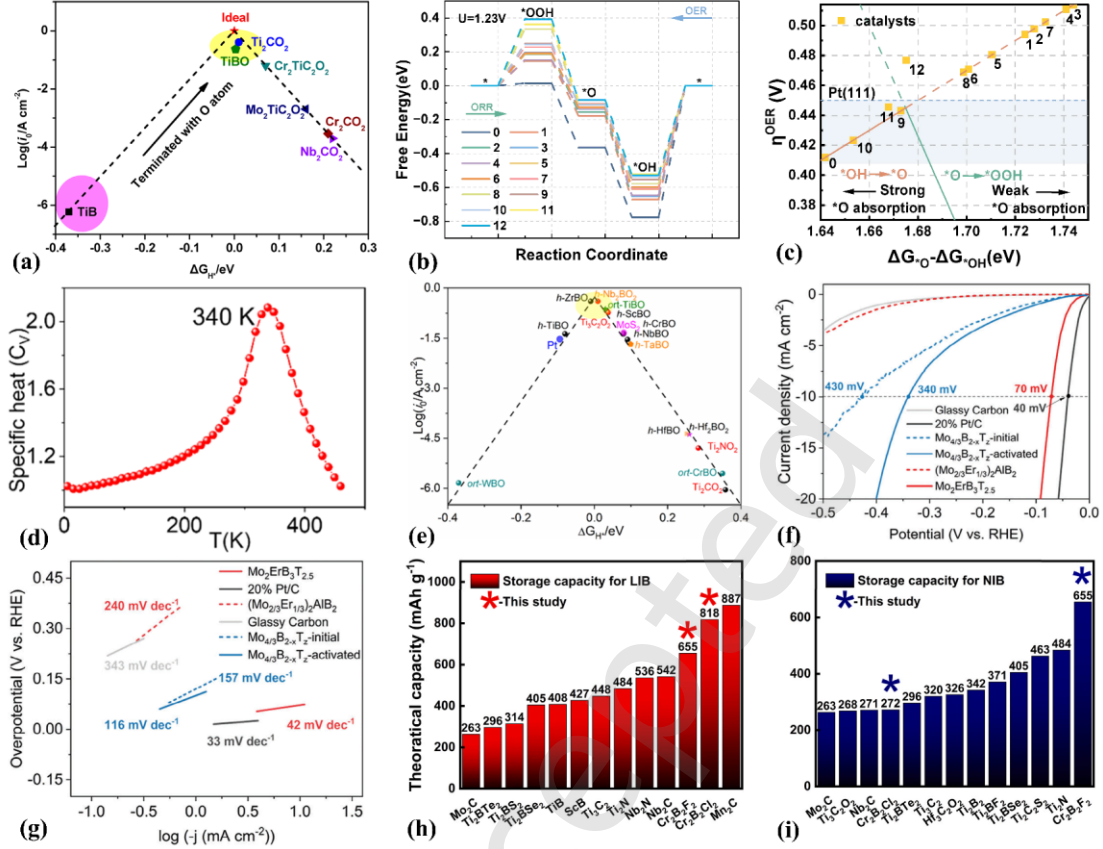


Fig. 7. Computational MBene studies and one experimental comparison: (a) TiB–O* HER descriptor [154]; (b,c) calculated Pt@Hf_{2-x}Zr_xB₂O₂ ORR/OER energetics [155]; (d,e) modeled h-MnB magnetism and HER trends [38]; (f,g) measured HER polarization and Tafel curves for Mo₂ErB₃T_{2.5} [28]; and (h,i) predicted Li/Na storage capacities of terminated Cr₂B₂ sheets [50]. Panels (f,g) are experimental; the other panels are calculations. Adapted with permission from Ref. [154] for (a), © American Chemical Society 2019; Ref. [155] for (b,c), © Royal Society of Chemistry 2026; Ref. [38] for (d,e), © American Chemical Society 2024; Ref. [28] for (f,g), © Wiley-VCH GmbH 2024; Ref. [50] for (h,i), © Elsevier B.V. 2024.

The hydrogen evolution reaction represents one of the earliest and most extensively examined applications of MBene-focused computational work. For the TiB MBene monolayer, Li et al. [154] assessed harmonic dynamical stability through phonon spectra and short-time thermal persistence through AIMD (5 ps at 1000 K), while band structure and PDOS analyses confirmed the metallic nature of bare TiB, with electronic states near the Fermi level mainly contributed by Ti-3d orbitals. ELF analysis further indicated a weakly delocalized surface electron state on bare TiB

(described as a two-dimensional electron gas in free space, 2DEG-FS [154]), which may contribute to the high surface reactivity toward hydrogen adsorption. Under electrochemical conditions, surface Pourbaix analysis indicated that fully oxidized TiB–O* is the dominant/stable surface state over a broad pH range and was therefore selected for subsequent HER calculations. As shown in Fig. 7(a), the corresponding volcano plot of exchange current density places TiB–O* near the peak with a near-zero average hydrogen adsorption free energy, $\Delta G_{H^*} \approx 0.03$ eV, outperforming most carbide-based MXenes (e.g., Nb₂CO₂) and showing comparable HER activity to Ti₂CO₂ [154].

The demand for catalysts capable of driving both oxygen reduction and evolution reactions has motivated computational exploration of MBenes in bifunctional electrocatalysis. To this end, Xue et al. [155] designed Pt single-atom catalysts (SACs) anchored on solid-solution Hf_{2-x}Zr_xB₂O₂ MBenes (Pt@Hf_{2-x}Zr_xB₂O₂). Formation and binding energy calculations, oxygen-vacancy formation energies, Pt anchoring energies, and AIMD simulations were used to evaluate the structural and thermal stability of the hexagonal-phase SACs. Pourbaix diagram analysis further suggested favorable electrochemical stability over a broad pH range. As shown in Fig. 7(b), Gibbs free-energy diagrams for the four-electron ORR and OER pathways identify the potential-determining steps for each catalyst. The OER volcano plot in Fig. 7(c) further reveals that the optimal composition, Pt@Hf_{1.375}Zr_{0.625}B₂O₂, lies near the optimal region, achieving an OER overpotential of 0.42 V, lower than that of IrO₂ (0.57 V), and an ORR overpotential of 0.54 V, comparable to that of Pt (0.45 V).

[155].

Computational investigations have also revealed that MBenes can simultaneously exhibit exceptional magnetic properties and catalytic activity within a single structural family. A systematic study by Miao et al. predicted 15 distinct *h*-MBene compositions, of which four (TiB, VB, CrB, MnB) were identified as antiferromagnetic metals [38,156]. As shown in Fig. 7(d), Monte Carlo simulations yielded Néel temperatures of 340, 310, 180, and 280 K for *h*-MnB, *h*-CrB, *h*-VB, and *h*-TiB, respectively, with *h*-MnB reaching a notable 340 K and thus highlighting its promise for antiferromagnetic spintronic applications [38]. Notably, the same family also includes promising HER electrocatalysts: among the 11 HER-active candidates, *h*-ZrBO, *h*-MoBO, *h*-ScBO, and *h*-Nb₂BO₂ lie close to the peak of the HER volcano curve, indicating superior catalytic performance compared with selected *ort*-MBenes and representative MXenes, as shown in Fig. 7(e) [38]. The study further demonstrates that biaxial strain can serve as an effective tuning parameter for modulating electronic structures, Néel temperatures, and HER activities across the *h*-MBene family [38].

The integration of machine learning (ML) with high-throughput first-principles calculations has opened a particularly powerful avenue for accelerating MBene discovery. Wang et al. [28] screened 15771 quaternary *h*-MAB phase candidates and identified 47 thermodynamically and dynamically stable compositions, with bonding analysis revealing that a subset of Mo-based phases could yield bimetallic in-plane ordered MBenes (*i*-MBenes) upon chemical etching. Here, the quaternary *h*-MAB phases serve as precursors for 2D *i*-MBenes, rather than being conventional bulk

i-MAB phases. These computational predictions directly guided the successful synthesis and exfoliation of $(\text{Mo}_{2/3}\text{Er}_{1/3})_2\text{AlB}_2$ into 2D $\text{Mo}_2\text{ErB}_3\text{T}_{2.5}$ ($\text{T} = \text{O}, \text{F}, \text{and Cl}$), and as shown in Fig. 7(f) and (g), the resulting material exhibits exceptional HER activity in 0.5 M H_2SO_4 , reaching 10 mA cm^{-2} at an overpotential of only 70 mV with a Tafel slope of 42 mV dec^{-1} , demonstrating the effectiveness of the ML-guided computational workflow [28].

Computational guidance has proven equally valuable in steering MBene development toward energy storage applications. Through DFT and AIMD simulations, Nirjhar et al. investigated F- and Cl-functionalized Cr_2B_2 MBenes as anode candidates for lithium-ion batteries (LIBs) and sodium-ion batteries (NIBs), confirming mechanical, thermal, and dynamic stability alongside intrinsic metallic conductivity, and demonstrating that surface functionalization significantly reduces Li/Na-ion diffusion barriers. As shown in Fig. 7(h) and (i), the calculated storage capacities are 818 mAh g^{-1} for Li in $\text{Cr}_2\text{B}_2\text{Cl}_2$ and 655 mAh g^{-1} for Na in $\text{Cr}_2\text{B}_2\text{F}_2$ [50].

Computational screening identifies composition-specific candidates and mechanisms for experimental testing, with the demonstrated parent–derivative pair in Ref. [28] providing one concrete example. The stability criteria summarized in Section 4.1.5, the elastic anisotropy in Section 4.2.2 and the thermal observables in Section 4.2.3 address different questions and do not rank all structural types by a single measure [61,63,65,120,121]. The synthesis routes in Section 5 and the measurements in Section 6 test which predictions survive the effects of processing,

defects, temperature and surface chemistry.

Just Accepted

Table 5. Overview of fabrication methods for MAB-phase materials: processing conditions, product forms, phase purity, relative density, yield availability, and application scope.

No.	Process Category	Synthesis Method	Selected Process Conditions	Reported Products and References	Product Form	Phase Purity, Density, Yield and Scope
1	Solid-state Reaction	Reaction Synthesis (pressureless sintering)	Composition-dependent temperature and dwell time; selected examples: Cr_2AlB_2 at 970 °C for 15 h under Ar; Fe_2AlB_2 at 1150 °C for 1 h under Ar.	Fe_2AlB_2 [94,157], MoAlB [158], WAlB [159], Cr_2AlB_2 [160], Cr_3AlB_4 [160], Mn_2AlB_2 [161], <i>i</i> -MAB $((\text{Mo}_{2/3}\text{R}_{1/3})_2\text{AlB}_2 (\text{R} = \text{Tb, Dy, Ho, Er, Tm, Lu, Y, Sc}))$ [11,25]	Powders; porous reaction bodies	P: Cr_2AlB_2 ~96–97 wt.%; Cr_3AlB_4 ~91–93 wt.% after selected reaction/purification sequences [160]; Fe_2AlB_2 >90 vol.% after 5 h milling and 1150 °C/1 h sintering under Ar (Fe:Al:B = 2:1:2) [157]. RD: Fe_2AlB_2 ~74% as reported (density 4.29 g cm ⁻³) [157]; Y: —. Product form and consolidation requirements depend on the preparation.

No.	Process Category	Synthesis Method	Selected Process Conditions	Reported Products and References	Product Form	Phase Purity, Density, Yield and Scope
2		Hot Pressing (HP)	1100–1600 °C; 30–60 MPa; selected holds 0.5–5.8 h [2,4,103]	Fe ₂ AlB ₂ [4,94], MoAlB [2], Mn ₂ AlB ₂ [95,162], MoAlB-0.15% Si [163]; MoAl _{1-x} Si _x B solid solutions [164], WAlB [71], Cr ₂ AlB ₂ [8], Cr ₄ AlB ₆ [8], (Mo,W)AlB solid solution [165], Fe ₂ Al _{1.15-x} B ₂ Ge _x Ga _x (x=0,0.05) [166]	Dense bulks	P: MoAlB with oxide/intermetallic residues [2]; Si-containing multiphase material [163]. RD: 94 ± 1% [2], 96.7% [103]. Y: —. Bulk mechanical/thermal specimens; texture and residual phases require checks.
3		Spark Plasma Sintering (SPS, FAST)	Selected examples: Cr ₂ AlB ₂ , 1000 °C/15 MPa/10 min plus NaOH [167]; Mo ₄ Y ₂ Al ₃ B ₆ , 1250 °C/30 MPa/10 min [168]	Cr ₂ AlB ₂ [167], MoAlB [169], WAlB [105], (Mo,W)AlB solid solution [5], <i>i</i> -MAB phases (e.g., Mo ₄ Y ₂ Al ₃ B ₆ [168], Mo _{4/3} Lu _{2/3} AlB ₂ [170]), related 211-type MAX boride Zr ₂ SB [97]	Dense bulks	P: 92.84 wt.% Mo ₄ Y ₂ Al ₃ B ₆ + 7.16 wt.% MoB; RD: 96.6% [168]. Cr ₂ AlB ₂ : qualitatively phase-pure after NaOH [167]. Y: —. Fine-grained bulk specimens. P: —; RD: —; Y: —.
4		Mechanical Alloying + Sintering/Hot Pressing (MA+HP)	Mechanical activation of powders, then consolidation; MoAlB example: HP at 1300 °C [6]	Fine-grained MoAlB [6]	Fine-grained dense bulks	MoAlB grain size 1.26 μm [6]. Powder activation followed by bulk consolidation; milling contamination and added processing time require evaluation.

No.	Process Category	Synthesis Method	Selected Process Conditions	Reported Products and References	Product Form	Phase Purity, Density, Yield and Scope
5	Molten Salt	Molten Salt Synthesis (MSS, MS ³ , MMS ³)	820–1200 °C; 0.5–6 h in selected reports; NaCl, NaCl–KCl or KBr media; Ar or salt-shielded air, depending on the study	Fe ₂ AlB ₂ [171], MoAlB [172], Mn ₂ AlB ₂ [173], WAlB [70,174], Cr ₂ AlB ₂ [175]	Powders after salt removal and, where used, chemical purification	P: WAlB 88.24 vol.% at 900 °C/2 h; Mn ₂ AlB ₂ 95.73 vol.% at 1000 °C/2 h [70]. MoAlB qualitatively phase-pure after HCl treatment [172]. RD: —; Y: —. Fine powder feedstock; washing/recovery must be included.
6	Self-propagating	Self-propagating High-temperature Synthesis (SHS)	Localized ignition; combustion wave lasts seconds; precursor mixing/activation and any subsequent densification are separate steps	MoAlB [176], Fe ₂ AlB ₂ [102,177], Mn ₂ AlB ₂ [178]	Powders, Porous sintered bulks	P: 99 wt.% Fe ₂ AlB ₂ after 10 min MA followed by SHS [177]. RD: —; Y: —. Powders or porous bodies; HP/SPS may be required for dense structural specimens.
7		Thermal Explosion Synthesis (TE)	Whole-body heating to ignition; furnace or SPS-assisted variants. The ignition temperature, reaction peak and applied pressure are distinct quantities	MoAlB [179–181], Hf ₂ SB [182], Zr ₂ SeB and Hf ₂ SeB [24], Fe ₂ AlB ₂ [183]	Powders, Bulks	P: 91.99 wt.% Hf ₂ SB in an SPS-furnace TE product [182]. RD: —; Y: —. Powders or reaction bodies; consolidation depends on the configuration. Hf ₂ SB is a related 211-type MAX boride.

No.	Process Category	Synthesis Method	Selected Process Conditions	Reported Products and References	Product Form	Phase Purity, Density, Yield and Scope
8		Self-propagating High-temperature Synthesis + Vacuum Arc Melting (SHS–VAM)	SHS of $\text{Fe}_2\text{O}_3/\text{B}_2\text{O}_3/\text{Al}$ precursors, followed by Al addition and vacuum arc melting [184]	Fe_2AlB_2 [184]	Bulks, powders	P: 47 and 61 wt.% Fe_2AlB_2 after VAM with 50% and 100% excess Al, respectively [184]. RD: —; Y: —. Oxide-based feedstock route; residual FeB and $\text{Al}_{3,25}\text{Fe}$ remain.
9	Vapor Deposition	Magnetron Sputtering (MS)	Cr–Al–B: room-temperature deposition, then Ar annealing at 650–800 °C [75]; MoAlB: 700 °C crystallization anneal [185]	Cr_2AlB_2 thin films [75], MoAlB thin films [185], $(\text{Mo,Cr})_2\text{AlB}_2$ thin films [186]	Substrate-supported thin films/coatings	P: Cr_2AlB_2 qualitatively phase-pure by XRD after annealing [75]. RD: —; Y: —. Film thickness, composition, adhesion and substrate compatibility are the relevant selection criteria.
10	Liquid Phase/Wet Chemical	Al-based Flux Method (Flux Method)	Excess Al flux; dissolution, controlled cooling and flux removal. Temperature and dwell/cooling schedule depend on composition [1,34,187]	$(\text{Mo,Cr})\text{AlB}$ single crystals ($0 \leq x \leq 0.4$) [34], $(\text{Mo,W})\text{AlB}$ single crystals ($0 \leq x \leq 1$) [34], Cr_2AlB_2 , Cr_3AlB_4 , Cr_4AlB_6 single crystals [1], WAlB single crystals [187], MoAlB single crystals [1]	Recovered individual single crystals	P: identified crystalline products [1,34,187]; numerical fraction —. RD: —; Y: —. Oriented crystals for intrinsic/anisotropic measurements; recovery and crystal dimensions require separate reporting.

No.	Process Category	Synthesis Method	Selected Process Conditions	Reported Products and References	Product Form	Phase Purity, Density, Yield and Scope
11		Hot-dip Aluminizing	750 °C; 30 min hot dipping, with study-specific post-treatment [188–190]	(Cr,Ti)-Al-B MAB phase coatings [188], Cr-(Al,Sn,Bi)-B solid solution coatings [189], Periodic layered structure (PLS) MAB phases [188], Cr-(Al,Zn)-B MAB phase [190], Cr-(Al,Si)-B MAB phase [190]	Surface coatings, Periodic layered structures	P: mixed MAB/intermetallic layers in periodic structures [188]; quantitative fraction —. RD: —; Y: —. Surface engineering; coating thickness, interfaces and phase distribution matter. P: MAB and Al ₂ O ₃ are major constituents; other borides/aluminides may remain [191]. Numerical fractions: —; RD: —; Y: —. Composite feedstock, with separation needed if a purified MAB parent is required.
12		Aluminothermic Reduction	Metal oxide + Al + B; exothermic reduction/reaction, with oxide-specific conditions [191]	Fe ₂ AlB ₂ /Al ₂ O ₃ composites [191], Cr ₂ AlB ₂ /Al ₂ O ₃ composites [191], MoAlB/Al ₂ O ₃ composites [191]	MAB/Al ₂ O ₃ composite products	

No.	Process Category	Synthesis Method	Selected Process Conditions	Reported Products and References	Product Form	Phase Purity, Density, Yield and Scope
13	High Pressure	High Pressure-High Temperature Sintering (HPHT)	Cr ₂ AlB ₂ : 1600 °C, 5 GPa, 1 h [192]	Bulk Cr ₂ AlB ₂ [192], MoAlB [193]	Bulk ceramic specimens	P: Cr ₂ AlB ₂ >94.5% (reported XRD/Rietveld estimate; mass/volume basis unspecified) [192]. RD: —; measured density: 5.26 g cm ⁻³ [192]; Y: —. Specialized bulk synthesis; pressure-cell dimensions and equipment constrain scale.
14		Reactive Hot Isostatic Pressing (RHIP)	Fe ₂ AlB ₂ : 1150 °C/4 h; 150 MPa during the final 2 h [194]	Bulk Fe ₂ AlB ₂ [194]	Dense bulks	P: single-phase by XRD, but microscopy detects Al-rich regions and residual B [194]. RD: —; Y: —. Bulk functional specimens.
15	Special Heating	Joule Heating Synthesis (JHS)	~930 °C for 12 s; vacuum < 200 Pa; carbon-felt Joule heater [195]. Excludes mixing, drying and cooling	(Fe _{1-x} Mn _x) ₂ AlB ₂ , sampled x = 0, 0.2, 0.4, 0.5, 0.7 and 1 [195]	Reaction compacts subsequently ground to powder	P: secondary phases remain [195]; quantitative fraction —. RD: —; Y: —. Functional powder demonstrated at 0.3 g precursor scale.

P: target-phase content or qualitative phase assessment; RD: relative density; Y: isolated product mass yield on the stated feed or theoretical basis. A dash (—) denotes unavailable quantitative data; qualitative phase-purity descriptions are retained as reported.

Phase contents retain the reported wt.% or vol.% basis and refer to the specified material and processing sequence. Reaction/hold times exclude other preparation steps unless stated.

5. Synthesis Methods for MAB Phases

This section compares routes for producing powders, consolidated bulk specimens, single crystals and substrate-supported films or coatings. Table 5 retains fifteen reported process variants and summarizes their conditions, product forms, phase assessments and application scope. Phase purity, relative density and isolated product yield describe different aspects of the product.

Precursor chemistry and thermal, pressure and atmosphere histories jointly control the reaction path and final microstructure. The discussion below emphasizes these processing variables and the state of the recovered product; mechanical and functional performance is discussed in Section 6. The reported phase fractions are examples tied to particular compositions and purification procedures, rather than route-wide purity limits. Table 5 and Section 5.8 compare the reported conditions and product forms of the principal techniques.

5.1 Solid-State Reaction Methods

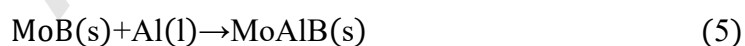
Powder reaction and consolidation are distinct operations that can be performed separately or combined. Pressureless reaction, hot pressing, SPS and mechanical activation followed by sintering differ in their heating and pressure histories; they do not all rely exclusively on conventional radiant heating or necessarily achieve simultaneous densification.

5.1.1 Reaction Synthesis

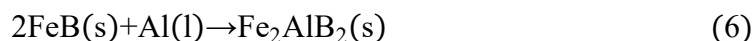
Reaction synthesis represents a simple and cost-effective route for MAB phase synthesis [1,3]. In a typical process, elemental or binary precursor powders are mixed,

cold-pressed into green compacts, and pressureless sintered under an inert atmosphere (Ar or vacuum) at temperatures typically ranging from 1000–1550 °C for minutes to several hours depending on the precursor system (commonly 1–2 h). This method has been widely used for the preparation of MAB-phase powders and porous bulk products.

The reaction pathways in solid-state reaction synthesis depend critically on the choice of starting materials. When binary borides are used in combination with elemental Al, the reaction path is generally simpler than that of elemental M–Al–B mixtures, because the preformed MB sublattice can react with, or be intercalated by, Al with fewer competing intermediate phases. For instance, Fuka et al. [196] demonstrated that predominantly single-phase MoAlB particulates could be obtained by pressureless sintering of MoB and Al powders in a molar ratio of 1:1.2 at 1000, 1250, and 1550 °C for 2 h under flowing Ar, following the overall reaction:



Similarly, Fe₂AlB₂ can be synthesized from FeB and Al powders through the overall reaction [197]:



In contrast, when elemental powders (M + Al + B) are employed as precursors, the reaction path becomes more complex, involving multiple intermediate phases [94,157]. Madhubala et al. studied the pressureless sintering of Fe₂AlB₂ from Fe, Al, and B elemental powders and considered the following possible intermediate reactions [157] :

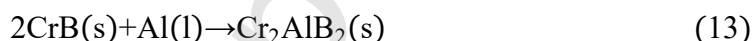


For elemental Fe–Al–B mixtures, the phase assemblage depends on composition, milling and sintering conditions. Madhubala et al. compared Fe:Al:B ratios of 2:1:2 and 2:1.5:2 at 1100, 1150 and 1200 ° C [157]. For the 2:1:2 mixture, 5 h of milling followed by pressureless sintering at 1150 ° C for 1 h under Ar produced a reported Fe₂AlB₂ volume fraction above 90%. The optimized product had a reported density of 4.29 g cm^{−3}, described by the authors as approximately 74% of the reference density. Phase fraction and densification therefore describe distinct outcomes of this preparation.

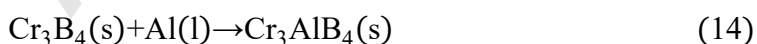
For comparison, the Cr-based preparations compiled in Ref. [160] reached approximately 96–97 wt.% Cr₂AlB₂ and 91–93 wt.% Cr₃AlB₄ using selected single-step reaction followed by NaOH purification or two-step reaction sequences. The contrast illustrates why precursor stoichiometry and post-reaction treatment accompany purity values in Table 5.

The mechanistic origin of the strikingly different reaction pathways between the binary boride + Al and elemental powder routes has been elucidated through high-temperature quenching studies by Hanner et al. [74]. Their work revealed two

fundamentally distinct formation mechanisms governed by the crystallographic relationship between the parent binary boride and the target MAB phase. For Cr-based MAB phases, the transformation proceeds via topotactic intercalation. In the CrB + Al system, molten Al atoms diffuse between the Cr–B layers of the parent CrB (*Cmcm* space group) and intercalate as an Al monolayer, with the Cr–B blocks shifting by $0.5(a + c)$ along [101] to accommodate the newly inserted layer, while the intralayer covalent bonding within the Cr–B slabs remains essentially intact. The reaction is a single step with no intermediate phases:



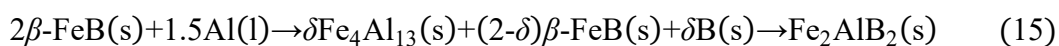
Similarly, Cr₃AlB₄ forms through an analogous topotactic sequence: CrB first reacts with B to yield CrB₂, then CrB and CrB₂ combine to form the Cr₃B₄ binary (*Immm* space group), and finally Al intercalates into the pre-formed Cr₃B₄ framework [74]:



In both cases, the parent boride structure serves as a direct template, the M–B bonding topology is preserved, and no Cr–Al intermetallics or Al–B compounds are detected as intermediates—rationalizing why the binary boride route yields exceptionally high phase purity for Cr-based MAB phases [74].

The formation of Fe₂AlB₂ from β-FeB and Al follows a fundamentally different, reconstructive pathway. Although β-FeB (*Pnma* space group) is structurally related to CrB as a twinned, distorted variant, Al does not directly intercalate into its lattice. Instead, at temperatures as low as 680 °C, Al preferentially reacts with Fe to form the

Fe₄Al₁₃ intermetallic, liberating free boron. At higher temperatures (~850–1050 °C), the remaining β-FeB and Fe₄Al₁₃ react with the previously expelled boron to crystallize Fe₂AlB₂ [74]:



The decomposition–reconstruction sequence is consistent with persistent Fe₄Al₁₃ impurities in the FeB + Al preparations examined in Ref. [74]. Equation (15) is retained as a schematic phase sequence with unspecified intermediate fractions; it is not an atom-balanced net reaction or a quantitative prediction of product yield. The contrast with the Cr-based examples concerns the studied precursors and conditions.

The contrasting Cr–Al–B and Fe–Al–B pathways in Ref. [74] provide a basis for precursor selection. Al excess, temperature and holding time can assist conversion, but their optimum values also depend on losses, competing phases and the required product form (Table 5).

Beyond the conventional MAB phases (such as Fe₂AlB₂, MoAlB, WAlB, Cr₂AlB₂, Cr₃AlB₄, seen in Table 5), reaction synthesis has proven effective for synthesizing in-plane chemically ordered *i*-MAB phases. Chong et al. [25] successfully prepared a series of (Mo_{2/3}R_{1/3})₂AlB₂ (R = Tb, Dy, Ho, Er, Tm, Lu) *i*-MAB phases via vacuum heating at 1400 °C, demonstrating the broad compositional flexibility of this technique. The primary advantages of reaction synthesis are its operational simplicity, low equipment cost, and suitability for bulk powder production. However, the products are typically porous and require subsequent grinding for powder applications or additional densification steps (e.g., hot pressing or SPS) for

bulk applications.

5.1.2 Hot Pressing

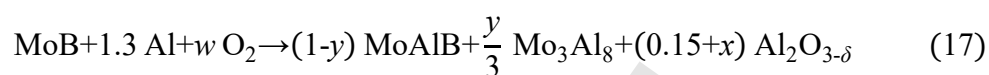
Hot pressing (HP) combines elevated temperature with uniaxial pressure to react and consolidate powders into bulk specimens. Selected reports use 1100–1600 °C and 30–60 MPa under vacuum or inert gas, with holding times from 30 min to several hours [2,4,103,198]. Applied pressure assists densification, but residual porosity, secondary phases and preferred orientation must be characterized for each body.

Kota et al. [2] prepared MoAlB by hot pressing MoB and Al powders at a 1:1.3 molar ratio, 1200 °C and 39 MPa for 5.8 h. The reported relative density was $94 \pm 1\%$. Microstructural analysis also identified oxide and intermetallic constituents. The overall reaction is:



Subsequent investigations have further refined the synthesis and consolidation strategies for MoAlB. Xu et al. [103] synthesized high-purity MoAlB powder from MoB and Al powders with an optimized MoB:Al ratio of 1:1.6 at 1100 °C, followed by HCl etching to remove excess Al and hot pressing at 1600 °C under 60 MPa for 1 h, achieving a relative density of 96.7 %. Zhang et al. [199] conducted a comprehensive study on the influence of Al excess, sintering temperature, and holding time on multiphase evolution in reactive-hot-pressed MoAlB ceramics. Their quantitative SEM analysis revealed that approximately 15–17 mol.% Al_2O_3 is commonly formed in MoAlB ceramics prepared from MoB and Al powders, arising from residual or absorbed oxygen in the starting powders, graphite mold, and possible

O₂ leakage during vacuum hot pressing. The Al-rich Al–Mo–B–O liquid phase formed during sintering was proposed to facilitate the direct layered conversion of MoB to MoAlB while also leading to the precipitation of Al₂O₃ and minor intermetallic Mo₃Al₈ phase. The multiphase evolution was described by:



Equation (17) records a proposed multiphase evolution involving variable phase fractions and oxygen content [199]. As written, it does not close the boron balance when the Mo₃Al₈ fraction is nonzero and should be read as a schematic phase relation, not a complete stoichiometric net reaction. Al excess was varied to control conversion and densification; the mechanical implications of the resulting sample differences are discussed in Section 6.1.

Hot pressing has been successfully extended to numerous other MAB phases, with Fe₂AlB₂ being consolidated either by reactive hot pressing of elemental Fe–Al–B powders or by hot pressing of FeB–Al precursor mixtures [4,94]. For example, Li et al. reported reactive hot pressing of elemental Fe, Al, and B powders with a molar ratio of 2:1.15:2 at 1200 °C and 30 MPa for 30 min, yielding Fe₂AlB₂ bulk samples [4]. Liu et al. further prepared dense Fe₂AlB₂ bulk by hot pressing a 1.1Al/2FeB mixture at 1100 °C under 30 MPa for 1 h [94]. Mn₂AlB₂ [95,162], MoAlB-0.15% Si multiphase ceramics [163], MoAl_{1-x}Si_xB solid solutions [164], WAlB [71], (Mo,W)AlB solid solutions [165], and Cr-based MAB phases (Cr₂AlB₂, Cr₄AlB₆) [8] have all been consolidated by hot pressing. Beckmann et al. [166] demonstrated reactive single-step hot pressing of Fe₂Al_{1.15-x}B₂Ge_xGa_x ($x = 0, 0.05$) MAB phases for

magnetocaloric applications. Beyond monolithic MAB-phase ceramics, hot pressing has also been employed to fabricate MAB-phase-reinforced composites. Zhang et al. [200] prepared MoAlB/carbon fiber co-reinforced copper matrix composites by hot pressing at 950 °C and 35 MPa. Their composite microstructure is discussed separately in Section 6.1.

The primary advantages of hot pressing include the ability to produce near-fully dense bulk samples suitable for comprehensive mechanical, thermal, and tribological characterization, broad applicability across diverse MAB-phase systems, and relatively good phase purity through parameter optimization. Limitations include restriction to simple geometries (typically discs or rectangular plates), potential grain coarsening due to extended holding times at high temperatures, residual impurity phases (intermetallics and oxides), and lower production throughput compared to pressureless sintering methods.

5.1.3 Spark Plasma Sintering

Spark plasma sintering (SPS), also termed field-assisted sintering technology (FAST), can consolidate MAB-phase ceramics using Joule heating of the die and, when electrically conductive, the specimen together with uniaxial pressure [198]. The achieved density and grain size depend on the powder and thermal history. Representative conditions and product assessments are summarized in Table 5.

Su et al. demonstrated the reactive SPS synthesis of high-density MoAlB bulk ceramics directly from Mo, Al, and B elemental powders in stoichiometric proportions. Heating at 50 °C/min to 1200 °C with a 10-min dwell time under 30 MPa

yielded samples with relative density exceeding 97 % [98,201]. The rapid processing effectively suppressed the formation of intermediate phases and minimized Al evaporation. Zhou et al. [202] further employed SPS combined with a hot-forging configuration to fabricate MoAlB bulk with strong grain preferred orientation, achieving a Lotgering orientation factor of 0.66 on the textured surface.

The SPS technique has proven particularly valuable for in-situ synthesis and densification of *i*-MAB phases, where precise control over stoichiometry and minimal impurity incorporation are critical. Du et al. [168] successfully fabricated Mo₄Y₂Al₃B₆ ceramics containing 92.84 wt.% Mo₄Y₂Al₃B₆ and 7.16 wt.% MoB from Mo, Y, Al, and B elemental powders by SPS at 1250 °C and 30 MPa for 10 min. The high relative density of 96.6 % and refined grain structure (mean dimensions of 3.47 μm × 0.90 μm) attested to the effectiveness of the SPS process. Similarly, high-purity, high-density Mo_{4/3}Lu_{2/3}AlB₂ *i*-MAB phase bulks were prepared from Mo, Lu, Al, and B powders at 1250 °C and 30 MPa [170]. For the Cr₂AlB₂ system, Demir and Ayas [167] employed SPS with coarse Cr and Al powders combined with nano-sized B powder and 50 % excess Al, holding at 1000 °C under 15 MPa for 10 min, and obtained phase-pure Cr₂AlB₂ after post-synthesis NaOH treatment to remove residual Al.

Other SPS examples include WAlB [105], (Mo,W)AlB solid solutions [5] and the related 211-type MAX boride Zr₂SB [97]. Short high-temperature exposure can limit grain growth or volatilization, but comparative density and properties depend on the specific specimen. Equipment cost, die dimensions, temperature measurement and

texture are practical constraints; electrical conduction through the specimen is not mandatory when heating is supplied through the tooling.

5.1.4 Mechanical Alloying Combined with Sintering or Hot Pressing

Mechanical alloying or activation increases contact between precursor constituents and can refine the powder before subsequent sintering. Milling conditions, contamination and reaction progress must be reported separately from the consolidation cycle. Gong et al. combined mechanical activation with hot pressing at 1300 °C for MoAlB [6].

The MA-assisted MoAlB material in Ref. [6] had an average grain size of 1.26 μm , illustrating the use of precursor activation for microstructure control. This route should be distinguished from the hot-pressed MoAlB-0.15% Si material in Ref. [163], which contained Si-doped MoAlB, $\text{Mo}(\text{Al},\text{Si})_2$ and ultrafine Al_2O_3 and is listed under HP in Table 5. The additive label does not specify a unique Si occupancy on the Al site.

5.2 Molten Salt Synthesis

Molten salt synthesis (MSS) uses a liquid salt medium to assist reaction and particle formation. Representative media include NaCl, NaCl–KCl and KBr, with salt loading, atmosphere and temperature selected for the particular precursor system [171–175]. Open-air operation applies to salt-shielded configurations; it is not a general property of every MSS experiment. The powder recovered after washing or further chemical purification must be distinguished from the as-reacted salt/product mixture.

Liu et al. obtained qualitatively phase-pure MoAlB powder using NaCl under Ar at 1000 °C for 6 h with 140% excess Al, followed by water washing and HCl purification [172]. Wang et al. prepared well-crystallized Cr₂AlB₂ powder from a Cr:Al:B precursor ratio of 2:2:2 at 1100 °C for 0.5 h under Ar, using NaCl–KCl and a salt-to-reactant mass ratio of 1:1 [175]. Small amounts of CrB and Al₂O₃ were identified qualitatively in the product.

A particularly significant advance was the development of the molten salt shielded synthesis/sintering (MS³) process by Dey et al. [173], which enables MAB phase synthesis in open air without the need for inert gas protection. In this approach, the precursor–salt mixture is pelletized and embedded within a salt bed, which upon melting forms a protective liquid barrier that shields the reactants from atmospheric oxygen. Using this method, high-purity Fe₂AlB₂, Mn₂AlB₂, and MoAlB powders were successfully synthesized in ambient air. Benamor et al. [171] extended this concept by incorporating Sn as an additive in the KBr molten salt system, enabling the synthesis of high-purity Fe₂AlB₂ powder at 1000 °C in open air with only 1 h holding time. The Sn additive was found to effectively lower the formation temperature of intermediate phases, thereby accelerating the overall reaction kinetics while the molten salt layer prevented oxidation.

Mondal et al. [174] developed a modified molten salt shielded synthesis (MMS³) method using a NaCl–KCl eutectic mixture to synthesize WAlB in an open atmosphere. With W:Al:B = 1:2.5:1, heating at 820 °C for 2 h followed by a 500 °C hold for 1 h yielded sub-micron particles (230–450 nm). The 88.24 vol.% WAlB

reported in the earlier salt-shielded preparation [70] belongs to a different condition: W:Al:B = 1:3:1 at 900 °C for 2 h. Through systematic investigation of intermediate phases, Mondal et al. [174] elucidated a template-growth formation mechanism in which W–Al intermetallic compounds (WAl₄, WAl₅, WAl₁₂) with layered particulate morphology first form at low temperatures (600–700 °C) and subsequently react with residual tungsten and boron at temperatures above 750 °C to form the layered WAlB MAB phase:



Roy et al. reported 88.24 vol.% WAlB at 900 °C for 2 h and 95.73 vol.% Mn₂AlB₂ at 1000 °C for 2 h using a modified molten salt shielded route [70].

MSS is relevant to powder feedstock production and, where selective etching has been demonstrated, preparation of parent powders for MBenes. Route selection must include the salt and purification chemistry, residual oxides or borides, particle morphology and product recovery. A lower reaction temperature or a short dwell alone does not establish a lower total process cost or higher mass yield.

5.3 Self-Propagating High-Temperature Synthesis and Related Combustion-Based Methods

Combustion synthesis methods exploit the highly exothermic nature of MAB phase formation reactions to achieve self-sustaining, rapid synthesis with minimal external energy input. Three distinct process variants have been developed, differing

in the mode of ignition and combustion propagation.

5.3.1 Self-Propagating High-Temperature Synthesis

In self-propagating high-temperature synthesis (SHS), local ignition initiates a combustion wave through a precursor compact; the subsequent reaction is sustained by its exothermic heat release [176,177,198]. The wave can traverse the compact within seconds, but mixing, mechanical activation, cooling and any consolidation are additional operations. Powder or porous reaction bodies should therefore be distinguished from dense ceramics obtained after HP or SPS.

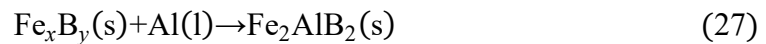
Yin et al. [176] first successfully prepared high-purity MoAlB powder within seconds using SHS. The adiabatic combustion temperature for the MoAlB formation reaction was calculated to be approximately 1949 K, satisfying the empirical criterion for self-sustaining combustion ($T_{ad} > 1800$ K). Potanin et al. [203] subsequently prepared MoAlB ceramics using SHS in a layered combustion mode combined with hot pressing (HP) at 1300 °C, systematically investigating the synthesis mechanism and the mechanical, thermophysical, and oxidation-resistant properties of the resulting ceramics.

Potanin et al. [177] obtained a product containing 99 wt.% Fe_2AlB_2 and 1 wt.% FeB by combining 10 min of mechanical activation (MA) with SHS. The study revealed that MA for 10 min enabled a steady-state layerwise combustion mode; most significantly, the Fe_2AlB_2 phase directly nucleated and crystallized from a boron-containing metallic melt without the formation of intermediate phases. The combustion temperature varied from 1110 to 1220 °C depending on the initial

temperature (T_0), and autoignition was recorded at $T_0 = 210$ °C. The heat release increased from 684 to 712 J/g as the MA duration was extended from 7 to 10 min, reflecting the enhanced energy storage through defect accumulation and increased reactive surface area. The ceramics produced in the layerwise combustion mode inherited the structure of the mechanocomposite, consisting of composite agglomerate particles sized up to 30 μm with grain sizes up to 2 μm . The proposed reaction pathway involves [177]:



Possible intermediate-mediated pathways are represented schematically in Eqs. (25)–(27) [177]. The variable intermediate formulas and omitted stoichiometric coefficients identify candidate phase connections; these expressions are not balanced net reactions and do not determine phase fractions or yields:



Merz et al. [178] successfully prepared high-purity Mn_2AlB_2 powder using induction furnace-assisted SHS, clarifying the influence of aluminum content (140 % of stoichiometric ratio), ball milling time (longer times, up to 120 min, being beneficial), and compaction pressure on product purity and reaction behavior. The

short combustion stage is a process advantage, although a comparison of total energy or throughput must include precursor preparation and subsequent consolidation. However, the products typically exhibit high porosity and relatively limited phase composition control, necessitating subsequent densification by hot pressing or SPS for structural applications.

5.3.2 Thermal Explosion Synthesis

Thermal explosion (TE) synthesis differs from SHS in that the entire green compact is uniformly heated in a furnace until it reaches the critical ignition temperature, at which point a violent exothermic reaction occurs simultaneously throughout the sample volume [179]. The temperature spikes from the ambient furnace temperature to the combustion temperature (often exceeding 1200 °C) within seconds, completing the elemental-to-MAB-phase transformation. The products are typically powders or porous bulks.

Liang et al. [179] pioneered the thermal explosion synthesis of MoAlB, demonstrating that ceramics with high MoAlB content could be prepared from Mo/Al/B powder mixtures in a conventional tube furnace at only 800 °C for 1 min. The reaction mechanism was elucidated through a combination of differential scanning calorimetry (DSC), XRD, and thermodynamic analysis. The process initiates with Al melting at approximately 665 °C, followed by exothermic reactions forming binary compounds:





These intermediate binary compounds subsequently transform into the ternary MoAlB phase through two primary reaction pathways: [179]

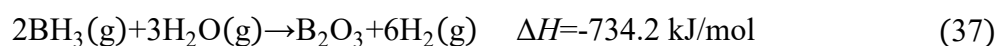


Additional contributions arise from reactions involving Mo_2B and AlB_2 : [179]



This team subsequently expanded this approach, using Mo, Al, and B_2O_3 as raw materials to synthesize high-content MoAlB ceramics with small amounts of Al_2O_3 and MoB impurities [180]. The addition of excess Al compensated for volatilization during the thermal explosion and promoted gaseous AlO formation, thereby suppressing solid Al_2O_3 synthesis and improving MoAlB yield.

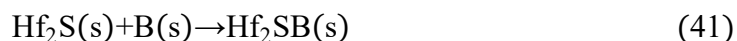
A novel variant of thermal explosion synthesis was reported by Teslia et al. [181], who synthesized pure-phase MoAlB powder by heating Mo, Al, and B elemental powders in a hydrogen atmosphere at 500–900 °C for 30 min. The hydrogen environment facilitated the formation of borane intermediates (BH_3 , B_4H_4), whose subsequent reaction with water vapor released extraordinarily high exothermic energy:





This enormous heat release caused local temperatures to spike to 2800–3000 °C, driving the complete conversion of refractory intermediate phases to single-phase MoAlB powder with equiatomic composition and elongated plate-like crystal morphology (250–500 nm thickness, 10–15 μm length). Post-synthesis heat treatment at 900 °C yielded the final product with lattice parameters $a = 3.2114 \text{ Å}$, $b = 13.9736 \text{ Å}$, $c = 3.1034 \text{ Å}$. [181]

Thermal explosion synthesis has also been applied to related sulfur-containing 211-type MAX borides. Zhang et al. [182] rapidly prepared Hf₂SB bulk material with 91.99 wt.% purity in an SPS furnace using thermal explosion, with Hf₂S identified as an intermediate. The expressions below distinguish competing HfB₂ formation (39) from the sulfide-mediated route (40)–(41); they are not a single sequential HfB₂-to-Hf₂SB pathway. Hf in these idealized expressions represents the metal available after dehydrogenation of the HfH₂ precursor [182]:



The TE method offers fast reaction speed, low energy consumption, and simple equipment requirements. However, the violent nature of the reaction presents challenges in terms of product porosity, process control, and the tendency to form impurity phases. Consequently, TE is often combined with hot pressing or SPS for the production of dense, high-performance materials.

5.3.3 Vacuum Arc Melting Combined with SHS

Atalay et al. first used oxide-based SHS to produce a FeB/Fe₂AlB₂ mixture and then added Al and applied vacuum arc melting (SHS–VAM) to increase the Fe₂AlB₂ fraction [184]. This approach provides an alternative to elemental metal feedstocks. Its suitability for functional specimens depends on the resulting phase assemblage, and an economic comparison must include processing, purification and recovery rather than assign a fixed percentage saving from the precursor choice alone.

5.4 Magnetron Sputtering for Thin-Film Deposition

Magnetron sputtering deposits material from compound or elemental targets onto a substrate in a vacuum chamber. Substrate temperature during deposition and subsequent crystallization annealing are separate process variables. The resulting film is assessed through composition, phase assemblage, thickness and its interface with the substrate, rather than by bulk densification criteria.

Jia et al. deposited Cr–Al–B films at room temperature and subsequently annealed them in Ar at 650–800 °C [75]. They obtained Cr₂AlB₂ films described as phase-pure by XRD, whereas the Cr₄AlB₄-containing films retained secondary phases. Zhang et al. prepared MoAlB films by DC magnetron sputtering followed by ex-situ annealing, with an Al target current of 0.8 A and a crystallization temperature of 700 °C among their selected conditions [185]. Pöllmann et al. investigated metastable (Mo,Cr)₂AlB₂ film formation by combining experiment and calculation [186].

Sputtering is relevant when the required product is a thin film or coating. Composition control, adhesion, substrate compatibility and deposition rate then matter

more directly than the relative density used for bulk ceramics. Multielement stoichiometry and secondary-phase formation remain processing constraints.

5.5 Liquid-Phase Methods

5.5.1 Aluminum Flux Method

Aluminum flux growth uses excess molten Al as a solvent and reactant to obtain individual crystals. The charge is heated for dissolution and then cooled according to a composition-specific schedule; the remaining flux is separated mechanically or chemically [1,34,187,198]. Crystal identity, dimensions and recovery are distinct from the phase fraction of an unseparated reaction batch.

Ade and Hillebrecht [1] were among the first to systematically employ this technique, growing single crystals of Cr_2AlB_2 , Cr_3AlB_4 , Cr_4AlB_6 , and MoAlB . The crystals exhibited platelet morphologies with lateral dimensions up to several millimeters and thicknesses on the order of tens to hundreds of micrometers, with the largest MoAlB crystals reaching dimensions of $9.3 \times 7.0 \times 0.3 \text{ mm}^3$. Shiotani et al. [204] recently achieved a milestone in MAB phase crystal growth by synthesizing $(\text{Fe}_{1-x}\text{Mn}_x)_2\text{AlB}_2$ single crystals across the entire Fe–Mn composition range ($0 \leq x \leq 1$) using the Al self-flux method. The initial composition $\text{Al}_5\text{Fe}_2\text{B}_{1.33}$ was heated to 1200°C for 3 h, then slowly cooled to 1080°C over 30 h before centrifugation to separate crystals from the flux. The resulting plate-like crystals reached dimensions of up to $5 \times 5 \times 0.2 \text{ mm}^3$ for Fe-rich compositions and $10 \times 1 \times 0.2 \text{ mm}^3$ for Mn-rich compositions. The resulting crystals enabled direction-dependent magnetic measurements and phase-diagram studies, as discussed in Section 6.2.

The flux method has been particularly instrumental in the discovery and characterization of *i*-MAB phases containing rare-earth elements. Tao et al. [26] synthesized the first single crystals of in-plane chemically ordered *i*-MAB phases with magnetic rare-earth elements, $\text{Mo}_{4/3}\text{RE}_{2/3}\text{AlB}_2$ (RE = Ho, Tb, Er), using the aluminum flux approach. Through a combination of STEM and XRD refinement, they precisely resolved the atomic structure of $\text{Mo}_{4/3}\text{Ho}_{2/3}\text{AlB}_2$, confirming in-plane Mo/Ho chemical ordering. Using vacuum pressureless sintering, Chong et al. [25] subsequently prepared the heavy-rare-earth series $\text{Mo}_{4/3}\text{RE}_{2/3}\text{AlB}_2$ (RE = Tb, Dy, Ho, Er, Tm, Lu), supplying structurally characterized parents for the studies discussed in Sections 6.2 and 6.6.

Flux growth supplies crystals for intrinsic and anisotropic measurements. Practical constraints include the growth and cooling schedule, crystal-size distribution, excess Al consumption and product recovery from the flux. Without a defined feed basis and recovered mass, crystal yield cannot be quantitatively compared with powder or bulk processing.

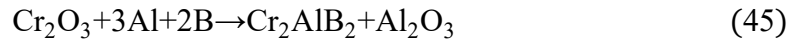
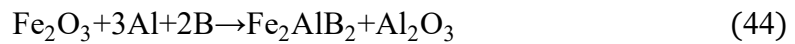
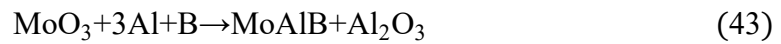
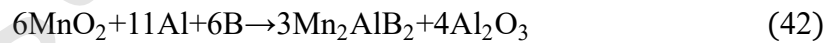
5.5.2 Hot-Dip Aluminizing

Hot-dip aluminizing is a surface engineering technique that enables the in-situ formation of MAB phase coatings on metallic substrates. The substrate (typically a Fe–Cr–B cast steel) is immersed in a molten Al-based alloy bath at 700–800 °C for minutes to hours, during which Al diffuses into the substrate and reacts with transition metal and boron species to form MAB phase layers. Zhang et al. [188,189] have systematically investigated this process for the Cr–Al–B system, demonstrating the

formation of Cr-(Al,Ti)-B MAB phase coatings when Ti is added to the Al melt, and Cr-(Al,Sn,Bi)-B solid-solution coatings when Sn and Bi are incorporated. A particularly intriguing finding was the formation of periodic layered structures (PLS) consisting of alternating MAB phase and intermetallic layers, whose periodicity could be tuned through the composition of the Al alloy bath [188]. Bi additives were found to suppress Sn whisker growth—a critical consideration for coating reliability [189]. These products are substrate-bound, often multiphase layers; bath additives do not by themselves establish substitution on one crystallographic site. Application performance depends on coating thickness, phase distribution and interface integrity.

5.5.3 Aluminothermic Reduction

Aluminothermic reduction combines metal oxides with Al and B. Al participates in oxide reduction and boride formation, while Al_2O_3 remains in the reaction product. Merz et al. [191] demonstrated composite formation in several MAB-phase systems, with representative reaction expressions written below:



Equations (42)–(45) are idealized, atom-balanced net reactions. The Al coefficients are 11, 3, 3 and 3, respectively. Al feed coefficients of 13.2 or 3.6 correspond to 20% excess relative to these net reactions; such excess can enter residual phases or be lost during processing. The multiphase products are discussed

below [191].

The products reported in Ref. [191] contain MAB and Al_2O_3 as major constituents, with additional borides, aluminides or oxides depending on the feed composition. This is a composite-production route rather than direct evidence of a purified MAB powder. Use as an etching precursor would require assessment of the oxide fraction, separability and effect of the residual phases on the recovered layered product.

5.6 High-Pressure Methods

High-pressure synthesis techniques employ GPa-level or several-hundred-MPa pressures to modify reaction thermodynamics, accelerate densification, and suppress undesirable phase transformations. Two distinct methods have been applied to MAB phase fabrication.

5.6.1 High-Pressure High-Temperature Sintering

High-pressure high-temperature (HPHT) sintering has been applied to MAB-phase ceramics. Jiang et al. prepared Cr_2AlB_2 bulk specimens from Cr and AlB_2 at 1600 °C and 5 GPa for 1 h [192]. The optimized specimen had a reported XRD phase-purity estimate above 94.5% and a measured density of 5.26 g cm^{-3} ; the corresponding mechanical data are discussed in Section 6.1. MoAlB is another reported example [193]. Pressure-cell dimensions and equipment requirements constrain the accessible specimen size, while phase content and density remain distinct measures of the product.

5.6.2 Reactive Hot Isostatic Pressing

Reactive hot isostatic pressing (RHIP) combines high-temperature reaction with gas pressure to consolidate MAB-phase ceramics. Da Igreja et al. prepared Fe_2AlB_2 at 1150 °C for 4 h, applying 150 MPa during the final 2 h [194]. The product appeared single-phase by XRD, but microscopy detected Al-rich regions and residual B. The magnetic response of this specimen is considered in Section 6.2.

5.7 Joule Heating Synthesis

Bai et al. used a carbon-felt Joule heater to heat precursor compacts at approximately 930 °C for 12 s under vacuum below 200 Pa [195]. The 30 MPa pressure reported in the preparation procedure was applied during cold compaction, not during the hot reaction. The short heating interval excludes powder mixing, drying and cooling and should not be presented as the duration of the entire preparation cycle.

The studied $(\text{Fe}_{1-x}\text{Mn}_x)_2\text{AlB}_2$ compositions had $x = 0, 0.2, 0.4, 0.5, 0.7$ and 1 [195]. Secondary phases remained in the products, and the cooled reaction compacts were ground into powders for electromagnetic characterization. The study used 0.3 g precursor batches. Its absorber performance is discussed in Section 6.2 with the powder/paraffin test configuration.

5.8 Summary and Process Selection Guidelines

For bulk mechanical and thermal specimens, HP or SPS can combine reaction and densification, but the achieved relative density must be reported alongside the phase assemblage and texture. Table 5 illustrates this distinction through MoAlB and

Mo₄Y₂Al₃B₆ examples [2,103,168]. MA can modify the precursor and grain size before consolidation [6], while HPHT and RHIP offer additional pressure regimes for selected compositions [192,194].

For powder feedstocks, reaction synthesis, MSS and combustion routes should be compared through phase content, particle morphology, purification and isolated recovery. SHS and TE have short reaction stages, whereas MSS can support powder formation within a salt medium; precursor preparation, washing and any later densification remain part of the complete process. Process-scale comparisons additionally require mass-yield and throughput data [70,160,172,177,182].

For intrinsic or anisotropic measurements, flux-grown single crystals provide a different specimen form from consolidated polycrystals [1,34]. Sputtering and hot-dip aluminizing instead serve substrate-supported films and coatings, where thickness, phase distribution, adhesion and substrate compatibility guide selection [75,185,188]. Aluminothermic composites and the Joule-heated powder series illustrate further product-specific options, with their recovery and scale still requiring separate assessment [191,195].

Overall, process selection should start from the required product form and compare phase content, density and recovery on a stated basis. For an MBene parent, these criteria must also include preservation of the required layered structure, residual-phase chemistry and evidence that the intended layers can be selectively removed without unacceptable reconstruction. Composition-specific etching evidence is discussed in Sections 5.9 and 6.6.

5.9 Synthesis Methods for MBenes

The synthesis of MBenes primarily involves three main categories: wet chemical etching, molten salt etching, and high-temperature dealloying [10,21,112]. These routes aim to remove selected A-layer species, drawing on the composition-dependent bonding discussed in Sections 3.2 and 4.2.1. The extent of removal, structural reconstruction, and final product form depend on the precursor and processing conditions.

Wet chemical etching includes acidic and alkaline treatments whose selectivity depends on the parent and reaction conditions. Zhang et al. reported an Al-depleted, layered CrB product after dilute-HCl treatment of Cr_2AlB_2 , describing it as a possible two-dimensional MBene [10,72]. For MoAlB , the LiF/HCl and NaOH treatments examined by Alameda et al. produced different degrees of Al removal, cavities and intergrowth structures [36,40]. For the ordered parent $(\text{Mo}_{2/3}\text{Y}_{1/3})_2\text{AlB}_2$, HF etching removes Al and Y, and subsequent delamination yields single-layer boridene $\text{Mo}_{4/3}\text{B}_{2-x}$ with surface terminations [11,17]. These are experimentally demonstrated sheets with ordered metal vacancies (*i*-MBenes) [11]. Figure 8 and Figure 9 contrast the reported CrB product and the structural characterization of boridene, respectively. The route overview in Fig. 10(a) illustrates wet chemical treatment.

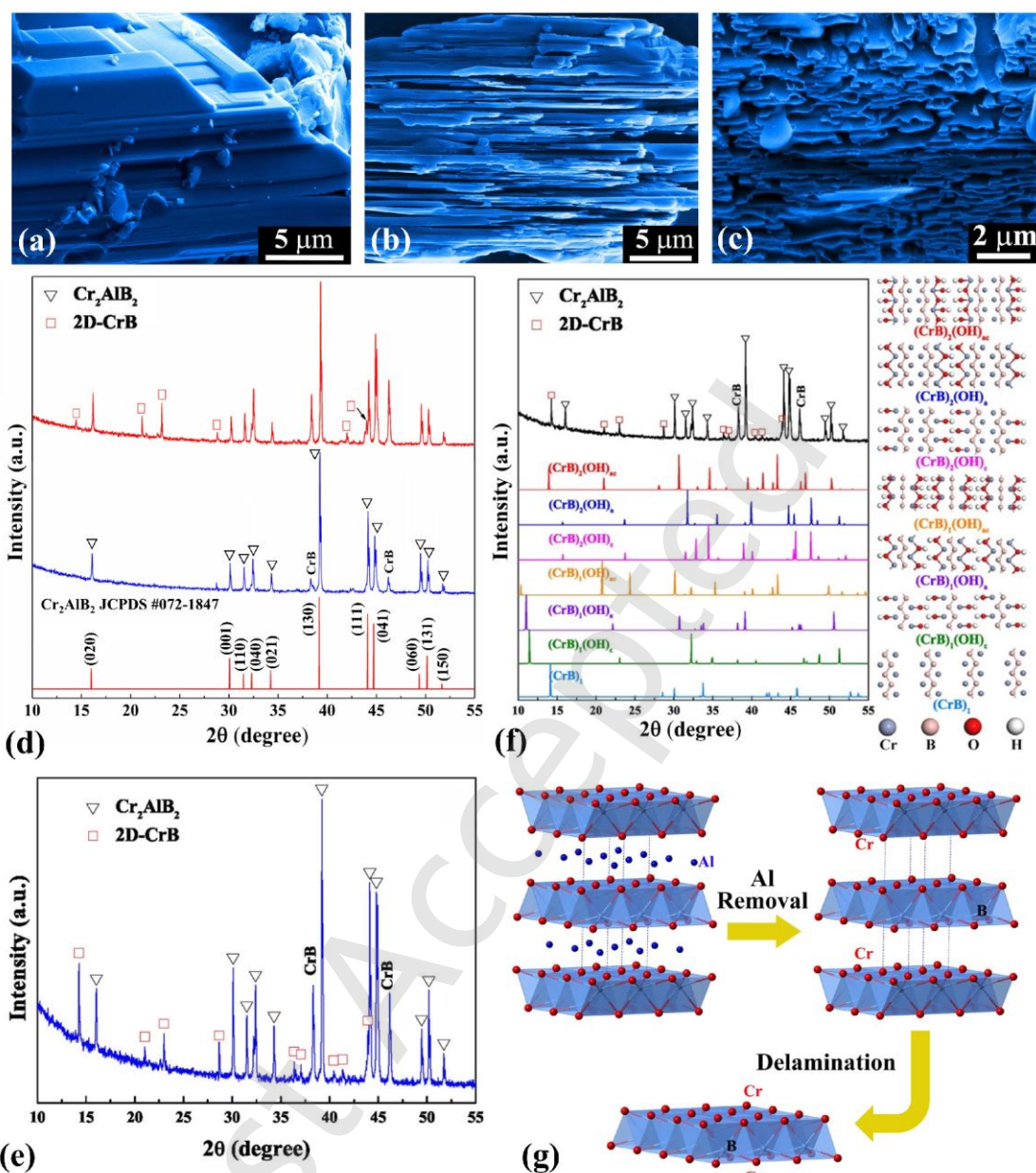


Fig. 8. Cr_2AlB_2 before and after dilute-HCl treatment: (a–c) morphology, (d–f) diffraction of the parent and reported layered CrB product, and (g) proposed structural transformation [10]. The layered CrB product was described as a possible MBene. Adapted with permission from Ref. [10], © Elsevier Ltd 2018, on behalf of the editorial office of Journal of Materials Science & Technology.

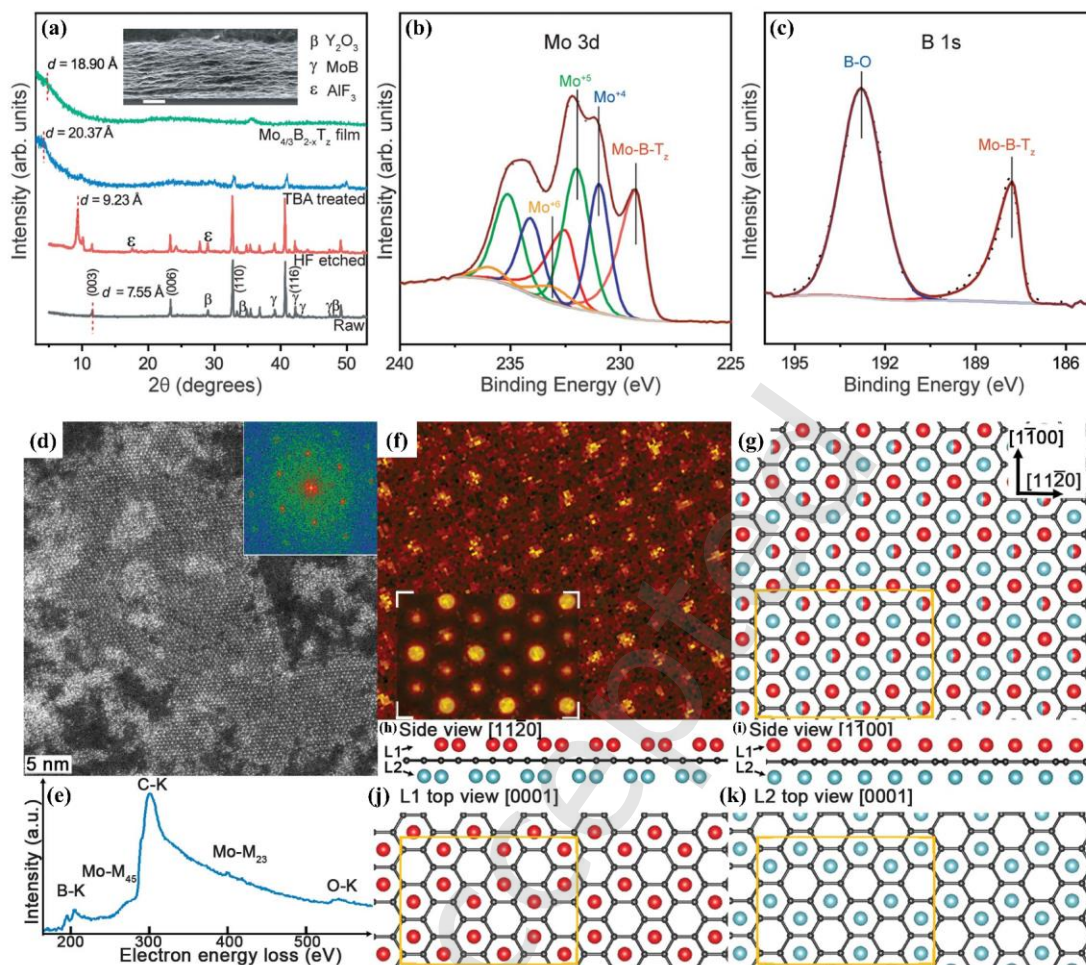


Fig. 9. Boridene derived from $(\text{Mo}_{2/3}\text{Y}_{1/3})_2\text{AlB}_2$: (a) XRD and cross-sectional SEM; (b,c) Mo and B XPS; (d) atomic-resolution STEM with a Fourier-transform inset; (e) electron-energy-loss spectrum; and (f – k) STEM and models of ordered metal vacancies [11]. Adapted with permission from Ref. [11], © The Authors 2021, exclusive licensee American Association for the Advancement of Science.

Bimetallic retention is a distinct outcome from the vacancy formation described above. Guided by ML and first-principles screening, Wang et al. synthesized the ordered parent $(\text{Mo}_{2/3}\text{Er}_{1/3})_2\text{AlB}_2$ and used HF/HCl treatment to retain both metals in $\text{Mo}_2\text{ErB}_3\text{T}_{2.5}$ ($\text{T} = \text{O}, \text{F}$ and Cl) [28]. The authors identify this experimentally obtained hexagonal derivative as a bimetallic *i*-MBene. This example links the screening in Section 4.3 to a demonstrated parent – product pair.

Alkaline treatment provides a fluorine-free route, although fluorine-free

processing is not unique to MBenes. Partial Al removal from MoAlB single crystals exposes catalytically active regions [40]. Atomic-resolution observations show double-to-single Al-layer conversion, intergrowths such as Mo₂AlB₂, further removal and local MoB sheets within etched regions [36]. Such local observations differ from recovery of a bulk population of free monolayers. Dilute NaOH at room temperature can instead yield multilayer MoAl_{1-x}B with incomplete Al removal [16]. Hydrothermal processing extends the accessible products: Xiong et al. reported accordion-like MoB using 25 wt.% NaOH at 150 °C [45], whereas Wei et al. used 0.25 M NaOH at 200 °C for 6 h, followed by ammonia-assisted sonication, to obtain material described as single/few-layer MoB [205]. Its O/OH surface chemistry must be distinguished from an ideal unterminated monolayer. The LiOH route further targets the passivating aluminum oxyhydroxide layer and produces a hydroxyl-terminated etched product [206]. Related topochemical studies examine other MAB-phase systems [207–210]. In each case, parent composition, residual Al, layer thickness and surface species are needed to identify the product.

Molten salt etching (Fig. 10(b)) uses a composition-specific redox reaction with Lewis acidic salts, followed by removal of salts and reaction by-products. It can provide a fluorine-free route, but preservation of the boride framework and the resulting surface chemistry require characterization. For MoAlB in ZnCl₂, Mou et al. reported stepwise removal through Mo₂AlB₂ at lower temperature, followed by further Al depletion and rearrangement at 700 °C to form 2D MoB nanosheets (MBenes) [112]. Using CuCl₂–NaCl–KCl salts, Chen et al. obtained an accordion-like

material at 620 °C and identified it as layered Mo_xB_y [49]. Electrochemical results are discussed in Section 6.6.2. Salt removal, residual metals, surface terminations and the measured layer-number distribution remain separate product-quality criteria.

Molten salts can also change which metal atoms and surface species remain. CuBr_2 treatment of $(\text{Mo}_{2/3}\text{Y}_{1/3})_2\text{AlB}_2$ produced a Br-bearing material reported as $\text{Mo}_{1.33}\text{Y}_{0.52}\text{B}_2\text{Br}_{1.22}$ [47]. The retained Y distinguishes this product from Y-depleted boridene, and its battery function is discussed in Section 6.6.3. For Mn_2AlB_2 , ZnCl_2 etching at a parent:salt molar ratio of 1:2 and 650 °C for 4 h produced thin-layer MnB nanosheets characterized by diffraction, spectroscopy and microscopy [29]. The associated magnetic response is discussed in Section 6.6.6. These examples show that salt selection and treatment conditions affect both residual composition and functional surface chemistry.

Lewis-acid molten-salt treatment of *h*-MAB Hf_2InB_2 in $\text{CuCl}_2\text{--NaCl--KCl}$ at 700 °C for 24 h under Ar removed In and yielded oxygen-terminated HfBO [84]. The characterized product included bilayer and multilayer regions as well as locally separated sheets, and contained approximately 20% HfO_2 . The lithium-storage results for this product are discussed in Section 6.6.2 [84].

High-temperature dealloying (Fig. 10(c)) operates in a solid-state, high-vacuum environment, utilizing the volatility of certain A-layer elements (e.g., In under the reported vacuum conditions) to selectively extract them from the MAB phase lattice. For Ti_2InB_2 , Wang et al. reported that immersion in 50% HF for 12 h at room temperature caused complete dissolution rather than selective In removal [21]. By

instead heating Ti_2InB_2 powder contained in a Mo tube within a dynamically evacuated quartz tube at 1050 °C for 6 days ($\sim 10^{-4}$ Pa) with SiC as an oxygen scavenger, In atoms were gradually extracted and deposited on the inner wall of the quartz tube, yielding a layered TiB product [21]. Notably, the resulting TiB possessed an orthorhombic structure (space group *Cmcm*) rather than the hexagonal symmetry of the parent Ti_2InB_2 . First-principles molecular dynamics (FPMD) simulations confirmed that at the high dealloying temperature, local displacements of Ti and B atoms drive a hexagonal-to-orthorhombic phase transition: the boron hexagonal rings collapse into one-dimensional zigzag chains characteristic of orthorhombic TiB, while the layered architecture is preserved through Ti–Ti metallic bonding between adjacent slabs [21]. The BET specific surface area increased from 2.45 to 6.16 $\text{m}^2 \text{g}^{-1}$ after dealloying [21]. The monolayer storage calculations are discussed separately in Section 6.6.2. The experimentally obtained layered TiB product contained TiB_2 and *Pnma* TiB impurities; the calculated monolayer capacity should therefore be distinguished from a measurement on that product [21]. This example shows that A-layer removal can be accompanied by structural reconstruction, rather than necessarily preserving the parent symmetry.

A useful synthesis-to-function sequence is therefore parent selection, selective removal or reconstruction, product identification, and testing of that identified product. Diffraction and elemental analysis establish phase and residual composition; microscopy and thickness measurements distinguish multilayer particles, few-layer sheets and isolated monolayers; surface analysis identifies terminations and oxidation

products. Section 6.6 uses these distinctions when comparing experimental devices with calculations on specified monolayers.

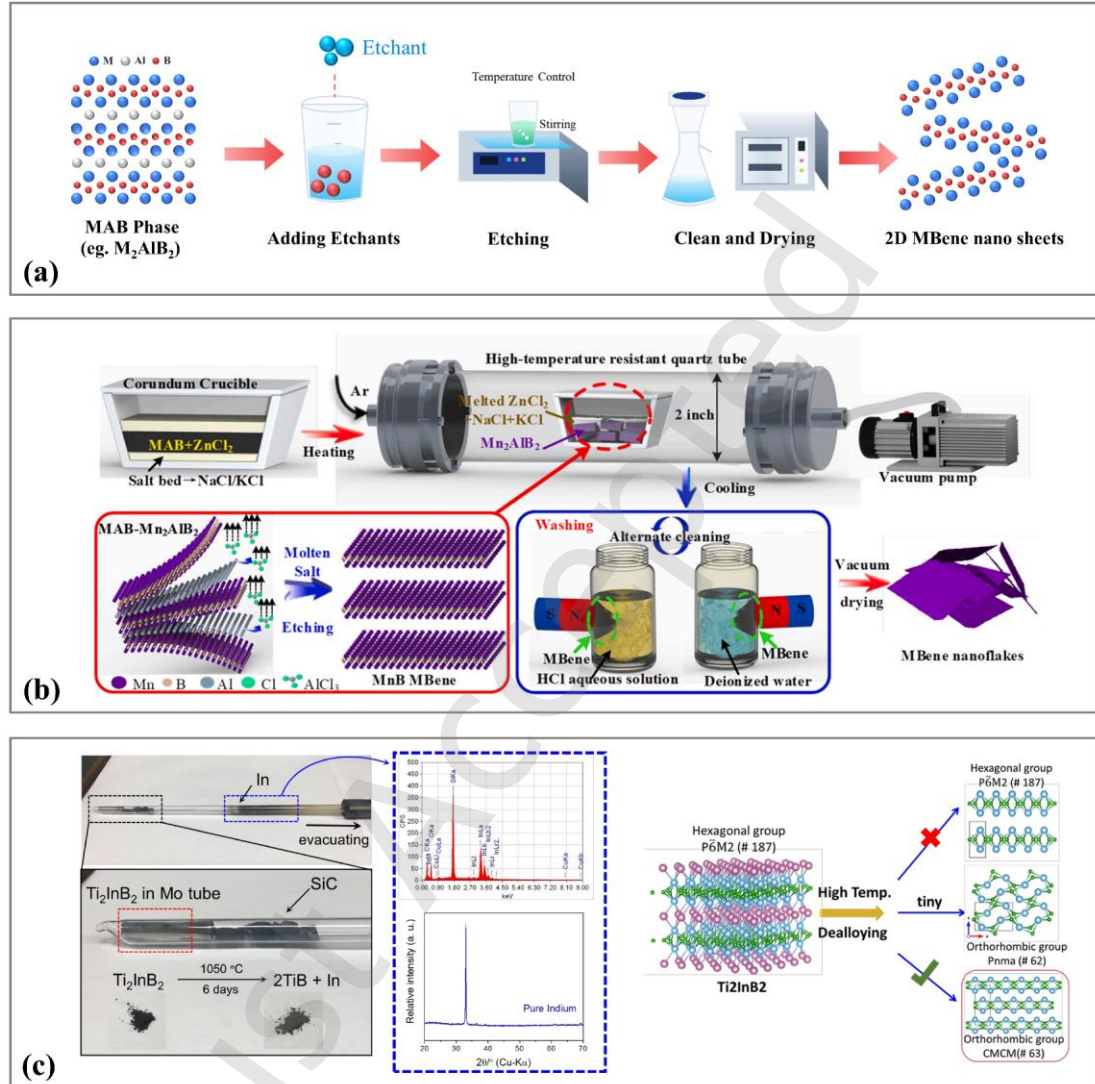


Fig. 10. Representative routes to etched boride products: (a) wet chemical treatment [10], (b) molten salt treatment [29], and (c) high-temperature dealloying [21]. Panel (a) is a schematic workflow; parent compositions and identified products are discussed in Section 5.9. Adapted with permission from Ref. [29] for (b), © 2025, published by Elsevier Ltd. Adapted from Ref. [21] for (c), © The Author(s) 2019, under CC BY 4.0 (<https://creativecommons.org/licenses/by/4.0/>); panels rearranged.

6. Properties and Application Fields of MAB Phases

As discussed in Section 3, many conventional MAB phases consist of transition-metal–boron structural units separated by A-containing layers. In these

phases, the contrast between relatively strong intralayer interactions and more compliant or chemically accessible A-related regions can contribute to a combination of stiffness, directional deformability, and damage-tolerant fracture [2–4]. The extent of this behavior varies with composition, crystal symmetry, boron-network topology, chemical ordering, phase purity, grain orientation, and sample densification. Related 211-type MAX borides and other non-Al subfamilies are therefore considered separately where their structures or measured properties differ from those of the conventional Al-containing phases. Figure 11 provides a guide to selected application areas, whose maturity and evidence differ by composition and product form. In Fig. 11, Ni_2B and $\text{Ti}_3\text{C}_2\text{T}_x$ are comparison materials; the Ti_2InB_2 electrode, MoAlB/Al laminate and formulated boride nanosheets represent different material states. Experimental measurements, proposed mechanisms and calculated activity must therefore be distinguished. ZBN – HA denotes hyaluronic-acid-functionalized zirconium boride nanosheets.

The selected bulk MAB phases reviewed here exhibit mechanical, transport, high-temperature, tribological [158,162], radiation-related [110,211], magnetic, and other functional properties. Some Al-containing phases form protective oxide scales [2,212,213], and MoAlB has demonstrated oxidation-induced crack healing under particular thermal-shock and oxidation conditions [7]. The following sections accordingly distinguish calculated predictions from experimental measurements and relate reported properties to composition, processing route, sample form, phase purity, microstructure, and testing conditions.

Selected MAB phases can also serve as precursors for MBenes [10,11,35,214].

The resulting two-dimensional materials extend the discussion from bulk structure–processing–property relationships to surface chemistry and nanoscale functionality. Section 6.6 distinguishes measured functions of identified products from predictions for specified monolayers.

Supplementary Table S1 compiles selected friction, oxidation, crack-healing and irradiation results with their material states and exposure conditions. It complements the mechanical and transport data in Tables 6 and 7.

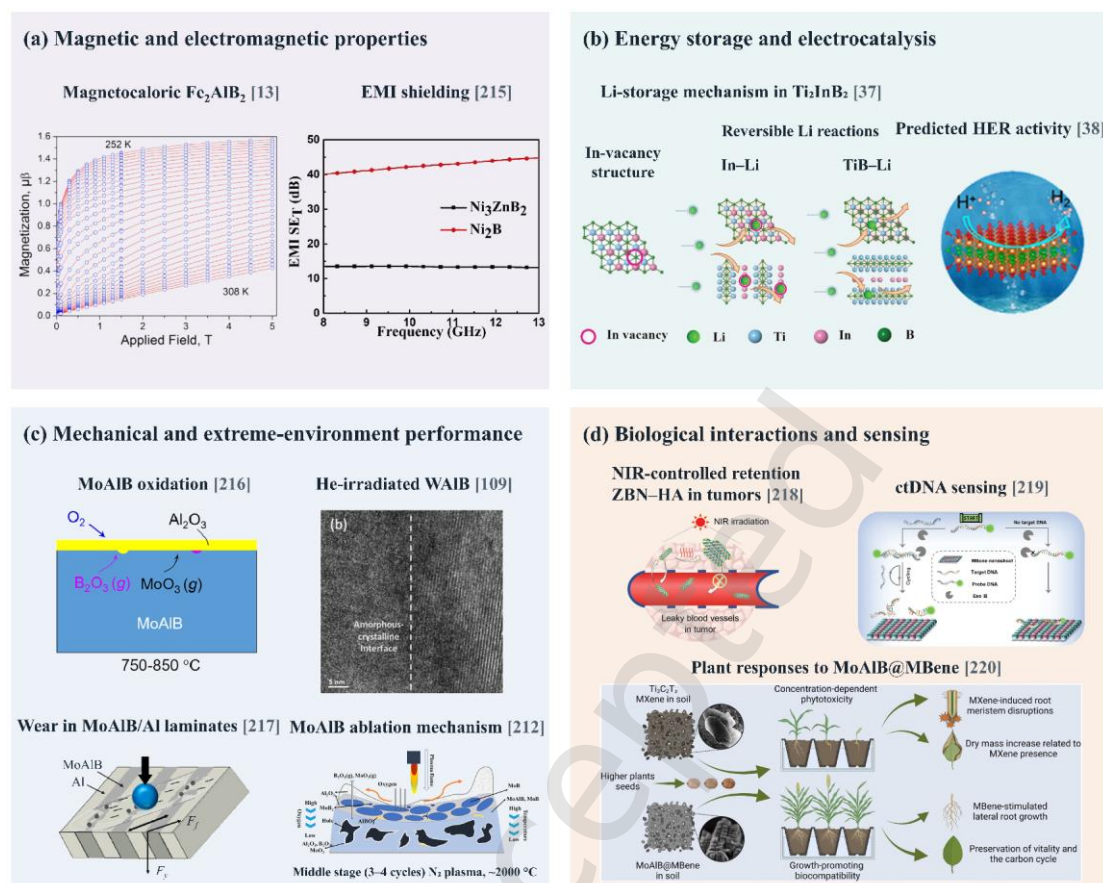


Fig. 11. Selected properties and applications of MAB phases and their derivatives. (a) Magnetization isotherms of arc-melted Fe_2AlB_2 (sample 1a, 252–308 K) [13] and $\text{Ni}_3\text{ZnB}_2/\text{Ni}_2\text{B}$ EMI shielding [215]. (b) Proposed Li-storage mechanism in Ti_2InB_2 [37] and predicted *h*-MBene HER activity [38]. (c) MoAlB oxidation [216], He-irradiated WAIB [109], MoAlB/Al wear [217], and the proposed middle-stage MoAlB ablation mechanism in nitrogen plasma [212]. (d) NIR-controlled tumor retention of ZBN-HA [218], Exo III-assisted MBene-based ctDNA fluorescence sensing [219], and plant responses to MoAlB@MBene and $\text{Ti}_3\text{C}_2\text{T}_x$ [220]. Material states and evidence are discussed in Section 6.

Source panels adapted from the indicated references. The magnetization plot corresponds to Fig. 5(a) of Ref. [13], also shown in its graphical abstract; the ctDNA schematic is the upper part of Scheme 1 in Ref. [219]. Adapted with permission from Ref. [13] for (a), © American Chemical Society 2013; Ref. [38] for (b), © American Chemical Society 2024; Ref. [216] for (c), © Elsevier B.V. 2020; Refs. [109] and [217] for (c), © Elsevier Ltd and Techna Group S.r.l. 2024 and 2020, respectively; Ref. [212] for (c), © Elsevier Ltd 2024; Refs. [218] and [219] for (d), © Wiley-VCH GmbH 2021 and 2024, respectively. Adapted from Ref. [215] for (a), Ref. [37] for (b) and Ref. [220] for (d), © The Authors 2023, 2024 and 2025, respectively, under CC BY 4.0 (<https://creativecommons.org/licenses/by/4.0/>). Ref. [13] is published under the ACS AuthorChoice License. Images have been cropped and rearranged for this review.

6.1 Mechanical Properties

Many experimentally studied MAB-phase ceramics combine substantial hardness or strength with non-catastrophic fracture behavior. To provide a transparent comparison with other layered ceramics and selected conventional ceramics, this review uses the damage-tolerance indicator

$$D_t = \left(\frac{K_{IC}}{\sigma_b} \right) \cdot \left(\frac{E}{H} \right)$$

following Bao et al. [93], where K_{IC} is fracture toughness, σ_b is bending strength, E is Young's modulus and H is hardness. D_t provides a semi-quantitative comparison of reported mechanical datasets.

D_t comparisons depend on matching material state and test conditions across the four inputs. Table 6 identifies representative moduli from separate sources and incomplete directional matching.

The D_t estimates complement experimental observations of non-catastrophic fracture, delamination, crack deflection, grain pullout, crack bridging and suppressed indentation cracking [4,93 – 95,98].

Within the Cr–B MAB-phase system, Cr_2AlB_2 has reported hardness values of 6–7 GPa for single crystals at 1 N [1] and 10.4 GPa for arc-melted and annealed bulk specimens at approximately 2 N [117], whereas Cr_3AlB_4 reaches 15–19.1 GPa under the same single-crystal conditions [1], a marked increase accompanying the higher boron content. The structural distinctions are summarized in Section 3.2. Zhou et al. predicted four possible slip systems for Cr_2AlB_2 , (100)[010], (010)[100], (010)[001], and (001)[010], compared with (010)[001] and (001)[010] for Cr_3AlB_4 and Cr_4AlB_6

[131]. These calculations suggest one route by which boron-network topology and the local environment near Al layers can influence deformation. They do not constitute direct observations of dislocation activity or establish that the number of possible slip systems alone determines hardness. The experimental composition–hardness trend reported by Ade and Hillebrecht [1] is therefore interpreted together with the loading and sample conditions in Table 6.

For MoAlB and WAlB, both of which share the 222-type structure (space group *Cmcm*), the reported Vickers hardness values vary appreciably with measurement conditions. For polycrystalline bulk samples measured under comparable loads, WAlB (11.45 GPa) is slightly harder than MoAlB (10.6 GPa) [2,103,105,211]; the single-crystal measurements also differ in sample state and indentation conditions (Table 6) [1]. Their related atomic structures [1,69] provide a basis for comparison, but the hardness difference alone does not establish a stronger W–B bond or isolate an orbital-size mechanism. The ideal-strength calculations in Ref. [128] instead provide a specific predicted failure pathway involving the Al–Al bilayers, as discussed in Section 4.2.2. Comparison with measured hardness requires consideration of density, microstructure, and indentation protocol.

Among the Al-containing 212-type M_2AlB_2 examples listed here, Fe_2AlB_2 exhibits an exceptionally high compressive strength of 2101 MPa (Table 6). The Si-containing MoAlB material in Ref. [163] reaches a reported 2620 MPa under its own processing and testing conditions; its additive-based sample designation is retained in Table 6. For the Fe_2AlB_2 specimen in Ref. [4], a flexural strength of 232

MPa gives an approximately 9:1 compressive-to-flexural strength ratio [4]. The compression-to-flexure contrast depends on loading mode, texture, porosity and failure mechanisms (Sections 3.2 and 4.2.1). As further evidenced by the load–displacement curve recorded during the single edge notched beam (SENB) test (Fig. 12(a)), Fe_2AlB_2 exhibits a noncatastrophic failure behavior characterized by a stair-stepping load–displacement response after the peak load, with a high work of fracture of 117 J/m^2 , indicating semi-stable crack propagation and additional energy absorption during crack extension [4]. The Vickers hardness of Fe_2AlB_2 shows a typical indentation-size effect, decreasing from approximately 14.7 GPa at 1 N to 10.2 GPa at 49 N (Fig. 12(b)), and notably, no dominant cracks are initiated from the corners of the Vickers indentation (Fig. 12(c)), indicating appreciable damage tolerance [4,94]. The high-magnification fracture surface of polycrystalline Fe_2AlB_2 (Fig. 12(d)) exhibits characteristic delamination and grain pullout features [94], which support energy dissipation by microstructural fracture processes. Using $E = 264.5$ GPa from Ref. [99] as a representative elastic modulus, the Fe_2AlB_2 data in Ref. [4] give a calculated D_I proxy of $0.565 \text{ m}^{1/2}$. This estimate is consistent with the fracture response in Ref. [4] and the separate delamination and grain-pullout observations in Ref. [94]. Polycrystalline Cr_2AlB_2 fabricated by the HPHT method exhibits a Vickers hardness of 9.9 GPa and a fracture toughness of approximately $5.3 \text{ MPa}\cdot\text{m}^{1/2}$ [192], demonstrating that the layered architecture endows this phase with an effective combination of hardness and damage tolerance. Mn_2AlB_2 , another 212-type phase, shows a hardness of 8.7 GPa and a compressive strength of 1240 MPa [95]. The BSE

image of the polished cross-section (Fig. 12(g)) reveals a dense microstructure with minor Al–Mn intermetallic and Al₂O₃ impurities, while the fracture surface after compressive failure (Fig. 12(h)) is dominated by cleavage and transgranular microcracking, with only occasional intragrain delamination [95].

For hot-pressed Fe₂AlB₂, Ref. [221] reports compressive strengths of 2082 MPa ($\perp$ HP) and 1992 MPa ($\parallel$ HP), and fracture toughnesses of 5.0 and 5.3 MPa·m^{1/2}, respectively (Table 6). These paired measurements describe anisotropy within the hot-pressed body. The corresponding D_t estimates use the representative scalar E identified in Table 6.

By comparison, MoAlB presents a different strength profile, with reported compressive and flexural strengths that vary substantially with sample processing and loading direction. For example, the calculated D_t proxies of 0.313 and 0.378 m^{1/2} listed for MoAlB combine the reported H , σ_b , and K_{IC} values from Refs. [98] and [103], respectively, with the representative $E = 372.9$ GPa reported in Ref. [152]. Their difference reflects measurements on differently processed and tested specimens. A fracture toughness of 5.45 MPa·m^{1/2} is reported for the specimen in Ref. [98]. As exemplified by the etched surface of MoAlB ceramic (Fig. 12(e)), the internal layered grain architecture with coexisting plate-like and layered-like morphologies provides a microstructural context for its reported mechanical response [98]. The fracture surface of MoAlB (Fig. 12(f)) further confirms a mixed mode of transgranular and intergranular fracture with clear laminar character, consistent with effective energy dissipation through multiple fracture pathways. These observations [98] complement

the calculated Al–Al compliance discussed in Sections 3.2 and 4.2.2.

The paired compressive strengths reported for hot-pressed MoAlB are 1940 MPa perpendicular to HP and 1420 MPa parallel to HP in Ref. [2], and 1620.2 MPa perpendicular to HP and 1252.7 MPa parallel to HP in Ref. [103] (Table 6). The differences between the perpendicular and parallel values reported for hot-pressed MoAlB primarily reflect crystallographic texture and loading direction in the hot-pressed body.

Machinability has been investigated in selected Al-containing MAB ceramics, and must be evaluated under the reported tooling and loading conditions. Kota et al. [95] systematically characterized the mechanical properties of dense polycrystalline Mn_2AlB_2 and reported that, while the material could not be machined with conventional high-speed steel tooling, solid carbide drill bits readily penetrated the surface to a depth of 1–2 mm before arresting (Fig. 12(i)). This partially machinable behavior is consistent with the moderate hardness and substantial compressive strength of Mn_2AlB_2 noted above (Table 6). The lower reference D_t values compiled for SiC and Si_3N_4 (0.113 and 0.180 $\text{m}^{1/2}$, respectively) [93] provide contextual estimates, but they do not on their own determine machinability under a given tooling and loading condition. For Si_3N_4 , processing and microstructure further limit comparisons across material grades [222]. The predicted slip systems of Cr_2AlB_2 [131] and the indentation-crack observations for Fe_2AlB_2 [4] concern different materials and types of evidence. Together with the Mn_2AlB_2 drilling test, they motivate further study of deformation and material removal; they do not establish low shear resistance

or ready machinability for every MAB-phase composition.

M-site substitution and chemical ordering provide distinct routes for modifying the mechanical properties of MAB phases (Table 6). The in-plane chemically ordered quaternary phases $\text{Mo}_{4/3}\text{Lu}_{2/3}\text{AlB}_2$ [170] and $\text{Mo}_{4/3}\text{Y}_{2/3}\text{AlB}_2$ [168] (*i*-MAB phases) exhibit hardness values of 10.29 and 10.81 GPa, compressive strengths of 1567 and 1255 MPa, and flexural strengths of 468 and 385 MPa, respectively, all comparable to those of MoAlB . Their reported fracture toughness values of 5.13 and 5.14 $\text{MPa}\cdot\text{m}^{1/2}$ are of the same order as the MoAlB results in Table 6; these cross-study data alone do not isolate the effect of M-site ordering. Further, the Vickers hardness values of $(\text{Mo,W})\text{AlB}$, $(\text{Mo,Cr})\text{AlB}$, and $(\text{Mo,W,Cr})\text{AlB}$ are 13.65, 12.72, and 13.37 GPa, respectively, all higher than that of MoAlB , whereas their fracture toughness values of 6.52, 5.88, and 6.40 $\text{MPa}\cdot\text{m}^{1/2}$ are below the 6.73 $\text{MPa}\cdot\text{m}^{1/2}$ reported for the SPS-processed MoAlB comparator [5]. The hardness improvements [5] indicate the potential of M-site substitution, but assigning them to stronger individual M–B bonds or modified interlayer bonding requires evidence beyond the hardness and toughness values alone.

MAB particles have also been examined as reinforcements in metal-matrix composites. In the carbon-fiber/Cu system studied by Zhang et al., the room-temperature tensile strength reached 269.8 MPa at 3.0 wt.% MoAlB addition, compared with 168.3 MPa for the corresponding composite without MoAlB [200]. This value describes the reinforced Cu composite; Table 6 summarizes bulk MAB-phase properties, and Section 5.1.2 describes the composite preparation route.

For MoAlB and Fe₂AlB₂, scatter among reports can arise from differences in density, residual Al₂O₃ or intermetallic phases, grain size, texture, precursor chemistry, sintering conditions and mechanical testing. Indentation load, fracture-toughness method and loading direction can affect the input properties independently, contributing to the spread in calculated D_t [4,94,98,102,103,163,221]. Overall, calculated D_t estimates for the selected MAB-phase reports in Table 6 span approximately 0.250–0.565 m^{1/2}. These values provide context for the fracture-energy dissipation mechanisms observed in selected MAB ceramics [4,93–95,98]. The combination of strong intralayer bonding and relatively compliant or chemically accessible A-related regions remains an important mechanistic basis for these behaviors in the representative Al-containing compositions discussed here. Its contribution depends on the individual structure and composition.

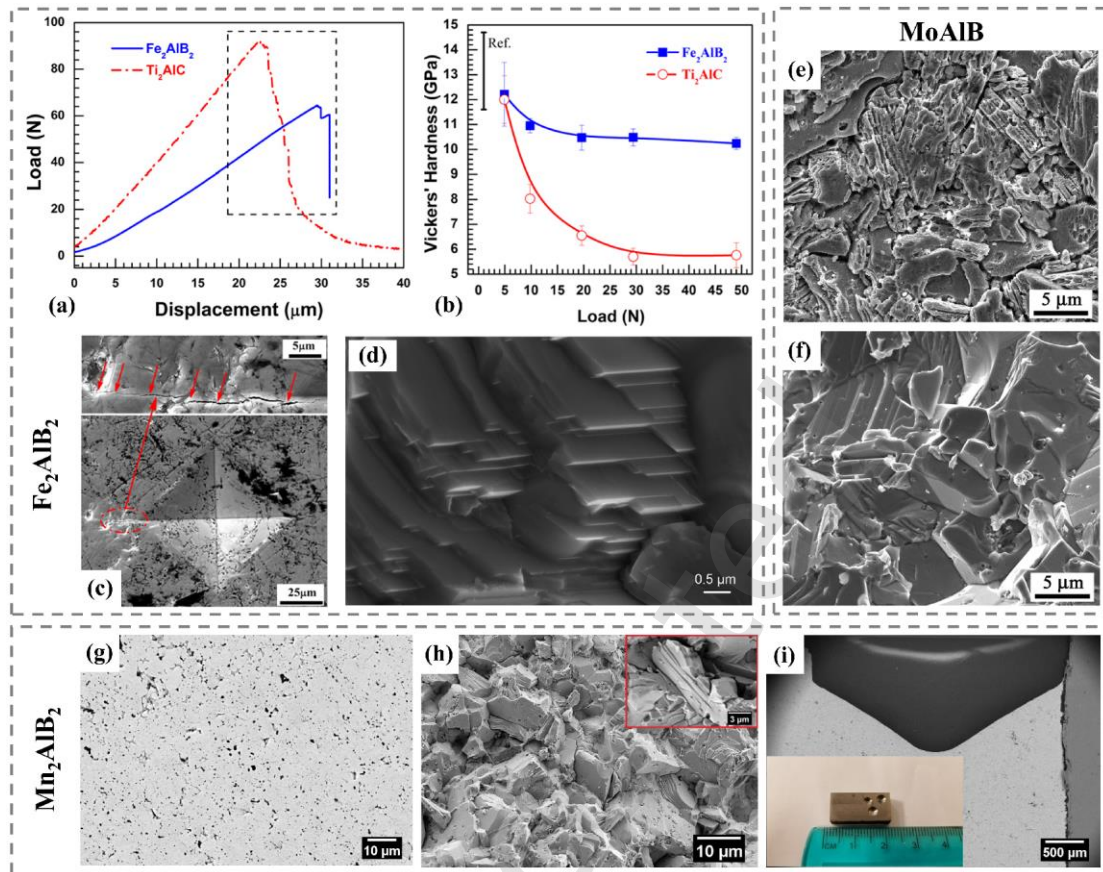


Fig. 12. Mechanical characterization grouped by material: (a–d) Fe_2AlB_2 —SENB loading, indentation hardness, indentation morphology and fracture surface [4,94]; (e,f) MoAlB —etched grains and fracture surface after sintering at 1200 °C [98]; (g–i) Mn_2AlB_2 —polished section, compressive fracture and drill impression [95]. Ti_2AlC is the reference in (a,b). Adapted with permission from Ref. [4], © The American Ceramic Society 2017, and Ref. [94], © Elsevier B.V. 2018, for (a–d); Ref. [98] for (e,f), © Elsevier Ltd and Techna Group S.r.l. 2020; Ref. [95] for (g–i), © Elsevier Ltd 2018.

Table 6. Mechanical properties and the semi-quantitative damage-tolerance indicator D_t of experimentally synthesized MAB-phase materials and selected ceramics. Mechanical inputs are reported at or near room temperature; D_t is calculated using reported or representative values. E : Young's modulus (GPa); H : Vickers hardness (GPa); σ_c : compressive strength (MPa); σ_b : bending strength (MPa); K_{IC} : fracture toughness (MPa·m^{1/2}); $D_t = \left(\frac{K_{IC}}{\sigma_b}\right) \cdot \left(\frac{E}{H}\right)$ (m^{1/2}). Indentation loads are given in parentheses. A dash indicates an unlisted value.

Materials	E (GPa)	H (GPa)	σ_c (MPa)	σ_b (MPa)	K_{IC} (MPa·m ^{1/2})	D_t (m ^{1/2})
MoAlB [98]	–	13.95 (10 N)	1467.6	465.8	5.45	0.313 ^a ($E = 372.9$ GPa [152])
MoAlB [2,152]	372.9	10.6 (0.98–9.8 N)	1940 (⊥HP) 1420 (HP)	–	–	–
MoAlB [103]	–	9.3 (30 N)	1620.2 (⊥HP) 1252.7 (HP)	456.4	4.3	0.378 ^a ($E = 372.9$ GPa [152])
MoAlB [164]	–	8.43 (mean over 9.8–196 N)	–	307	4.9	–
MoAl _{0.97} Si _{0.03} B [164]	–	14.89 (mean over 9.8–196 N)	–	385	4.77	–
MoAlB-0.15% Si [163]	–	14.2 (10 N)	2620	518.5	7.01	0.355 ^b ($E = 372.9$ GPa [152])
Mo _{0.75} W _{0.25} AlB [211]	–	12.3	–	287	–	–
Mn ₂ AlB ₂ [95]	243.0	8.7	1240	–	–	–
Fe ₂ AlB ₂ [4]	–	10.9 (9.8 N)	2101	232	5.4	0.565 ^a ($E = 264.5$ GPa [99])
Fe ₂ AlB ₂ [94]	–	10.7 (9.8–196 N)	–	336.9	4.6	0.338 ^a ($E = 264.5$ GPa [99])
Fe ₂ AlB ₂ [221]	–	10.4 (9.8 N)	2082 (⊥HP) 1992 (HP)	242	5.0 (⊥HP) 5.3 (HP)	0.525 ^{ac} (⊥) / 0.557 ^{ac} () ($E = 264.5$ GPa [99])
Fe ₂ AlB ₂ [99]	264.5	–	–	–	–	–
Fe ₂ AlB ₂ [102]	–	12.8 (98 N)	–	429	5.2	0.250 ^a ($E = 264.5$ GPa [99])
Cr ₂ AlB ₂ [1,117]	–	6–7 (1 N, single crystals); 10.4 (~2 N, bulk)	–	–	–	–
Cr ₂ AlB ₂ [192]	379.1– 434.5	9.9 (9.8 N)	–	–	5.3	–
Cr ₃ AlB ₄ [1]	–	15.0–19.1 (1 N, single crystals)	–	–	–	–
Cr ₄ AlB ₆ [1]	–	–	–	–	–	–

Materials	E (GPa)	H (GPa)	σ_c (MPa)	σ_b (MPa)	K_{IC} (MPa·m ^{1/2})	D_t (m ^{1/2})
WAlB [1]	—	21.7 (1 N, single crystals)	—	—	—	—
WAlB [105]	—	11.45 (10 N)	—	371.3	4.97	—
Mo _{4/3} Lu _{2/3} AlB ₂ [170]	—	10.29 (10 N)	1567	468	5.13	—
Mo _{4/3} Y _{2/3} AlB ₂ [168]	—	10.81 (10 N)	1255.14	384.82	5.14	—
Mo _{4/3} Sc _{2/3} AlB ₂ [20]	—	—	—	—	—	—
Hf ₂ InB ₂ , V ₃ PB ₄ , Hf ₂ PbB [84]	—	—	—	—	—	—
Ti ₂ InB ₂ [21]	—	—	—	—	—	—
Zr ₂ SeB, Hf ₂ SeB [24]	—	—	—	—	—	—
Zr ₂ SB [97]	—	12.55 (10 N)	2166.74	269	3.94	—
Hf ₂ SB [22]	—	—	—	—	—	—
Nb ₂ SB [100]	—	11.89 (10 N)	1157	249	4.76	—
Ti ₃ AlC ₂ [92,93]	288	3	764	340	6.9	1.948
Ti ₃ SiC ₂ [93]	310	4	—	436	7	1.244
Al ₂ O ₃ [223]	416	15	3000	380	3.5	0.255
ZrO ₂ [93]	200	13	—	950	12	0.194
SiC [93]	415	32	—	356	3.1	0.113
Si ₃ N ₄ [93]	300	15.5	—	700	6.5	0.180
ZrB ₂ [224]	490	22	—	565	3.8	0.150

^a E from a separate reference for the same nominal composition.

^b Parent-phase E : undoped MoAlB [152] used for MoAlB-0.15% Si [163].

^c Incomplete direction matching; Fe₂AlB₂ [221] also uses E from Ref. [99].

Comparison-ceramic inputs follow Ref. [93], except the evaluated Al₂O₃ dataset [223] and representative ZrB₂ values [224]; these compilations do not establish same-specimen matching.

6.2 Physical Properties and Potential Applications

Selected experimentally prepared MAB-phase materials combine electrical conduction with a range of thermal conductivities and expansion coefficients (Table 7). These measurements complement the ideal-crystal calculations in Section 4.2.3 and motivate evaluation of specific compositions as conductive components, coatings, magnetic refrigerants or electromagnetic absorbers. Their suitability depends on product form, thermal cycling and the operating environment.

The reported coefficients of thermal expansion (CTEs) vary with composition and measurement interval: MoAlB exhibits a CTE of $9.5\text{--}10.1 \times 10^{-6} \text{ K}^{-1}$ [2,98], while WAlB and the *i*-MAB phases $\text{Mo}_{4/3}\text{Lu}_{2/3}\text{AlB}_2$ and $\text{Mo}_{4/3}\text{Y}_{2/3}\text{AlB}_2$ present values of 9.15, 8.57, and $8.38 \times 10^{-6} \text{ K}^{-1}$, respectively [105,168,170]. The 211-type MAX-phase borides Zr_2SB and Nb_2SB display slightly lower CTE values of 7.64 and $7.1 \times 10^{-6} \text{ K}^{-1}$ [97,100]. In contrast, Mn_2AlB_2 shows a notably higher CTE of $18.6 \times 10^{-6} \text{ K}^{-1}$ [95]. For scale, the experimental Ti_3AlC_2 comparison summarized in Ref. [96] gives a mean linear CTE of approximately $9.0 \times 10^{-6} \text{ K}^{-1}$ over 100–1000 °C for the Ti_3AlC_2 constituent of a multiphase specimen. This material-specific benchmark does not establish coating/substrate compatibility, which requires expansion over the same temperature interval and the actual substrate composition. This thermal expansion compatibility is of considerable engineering significance for coating applications: Kota et al. [2] demonstrated that the excellent adhesion of the protective alumina scale formed on MoAlB during high-temperature oxidation can be partially attributed to the closeness of its CTE ($9.5 \times 10^{-6} \text{ K}^{-1}$) to that of $\alpha\text{-Al}_2\text{O}_3$

($8.5 \times 10^{-6} \text{ K}^{-1}$), thereby suppressing scale spallation under thermal cycling conditions. The cyclic-oxidation observations discussed by Xu et al. [103] concern the tested MoAlB material and surface scale; they do not establish adhesion or lifetime of a deposited coating on a turbine substrate. Combined with its inherent damage tolerance, indicated by the absence of dominant cracks around Vickers indents [2], MoAlB and related MAB phases are attractive candidates for high-temperature protective coatings on turbine components and other hot-section engineering structures.

As summarized in Table 7, MAB phases exhibit both metallic-level electrical conductivity and moderate thermal conductivity, with substantial variation across compositions. For the MoAlB reports listed here, the room-temperature thermal conductivity varies, ranging from 29.21 to 37.56 $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ depending on processing conditions [98,103], consistent with its high electrical conductivity ($2.0\text{--}2.9 \times 10^6 \text{ S} \cdot \text{m}^{-1}$) [98,103]. Compared with conventional ceramics, MoAlB exhibits relatively high electrical conductivity; however, for electrical heating applications, the key requirement is a balanced electrical resistivity rather than maximum conductivity. Electrical resistance depends on specimen geometry as well as resistivity; the reported thermal conductivity provides a starting point for evaluating temperature gradients in a designed element. Combined with the formation of a protective Al_2O_3 scale at 1300–1400 °C, these properties make MoAlB a promising candidate for high-temperature electrical heating components in oxidizing environments. In addition, the high electrical conductivity of MoAlB ($\approx 2.0\text{--}2.9 \times 10^6 \text{ S} \cdot \text{m}^{-1}$) suggests potential utility in electromagnetic interference (EMI) shielding and as conductive ceramic components

(e.g., high-temperature electrodes, electrical contacts) for demanding environments where polymer- and metal-based shields would fail due to thermal degradation or oxidation.

A quantitative MAX comparison is provided by the Ti_3AlC_2 -based specimen studied by Vovk et al. [104], whose total thermal conductivity is approximately $17 \text{ W m}^{-1} \text{ K}^{-1}$ near 300 K. The specimen was consolidated by spark plasma sintering and contained 96.65 vol.% Ti_3AlC_2 and 3.35 vol.% TiC ; conductivity was measured by a uniaxial stationary heat-flow method. For context, the MoAlB values of 29.21 and $37.56 \text{ W m}^{-1} \text{ K}^{-1}$ in Table 7 were obtained at room temperature for hot-pressed and spark-plasma-sintered bodies with relative densities of about 96.7% and 97.1%, respectively [98,103]. The latter measurement was parallel to the SPS loading direction. Comparison of these total conductivities must account for phase content, defects, density, heat-flow direction and measurement method.

Fe_2AlB_2 has lower reported thermal conductivity in the selected measurements: $7.5 \text{ W m}^{-1} \text{ K}^{-1}$ for the hot-pressed material [99] and $7.47 \text{ W m}^{-1} \text{ K}^{-1}$ for the combustion-synthesized specimen [102], with electrical conductivities of $0.37\text{--}0.62 \times 10^6 \text{ S m}^{-1}$. Electronic structure and magnetic order can affect transport, but density of states alone does not determine conductivity. Carrier velocities and scattering, lattice transport, impurities and porosity can all contribute to the $\text{MoAlB}/\text{Fe}_2\text{AlB}_2$ contrast. The coupled experimental/DFT study of Fe_2AlB_2 [99] and the heat-capacity/expansion modeling in Ref. [121] further show the dependence on magnetic state and temperature.

Beyond its transport properties, Fe₂AlB₂ has attracted considerable attention as a promising room-temperature magnetocaloric material. The magnetocaloric effect (MCE) in Fe₂AlB₂ originates from a second-order ferromagnetic–paramagnetic phase transition near room temperature, where the magnetization undergoes a rapid yet continuous change with temperature. This transition gives rise to a substantial magnetic entropy change ($-\Delta S_m$) when an external magnetic field is applied or removed. Tan et al. [13] first reported the MCE in Fe₂AlB₂ in 2013, measuring a maximum $-\Delta S_m$ of 4.1 J·kg⁻¹·K⁻¹ at 2 T and 7.7 J·kg⁻¹·K⁻¹ at 5 T in samples prepared by annealing in Ga flux, with these samples showing a Curie temperature of 307 K. This represented the largest isothermal entropy change near room temperature for any metal boride at that time. For bulk polycrystalline Fe₂AlB₂, Bai et al. [99] obtained a Curie temperature of 301 K with $-\Delta S_m$ values of 1.51 and 3.05 J·kg⁻¹·K⁻¹ at 2 T and 5 T, respectively. Potanin et al. [102] further demonstrated that Fe₂AlB₂ fabricated by combustion synthesis followed by hot pressing exhibits a Curie temperature of 291 K and a ΔT_a^d of 0.92 K at 1.8 T. The variation in MCE performance across different synthesis routes highlights the sensitivity of the magnetocaloric response to processing-dependent phase purity, grain morphology, and microstructure. From a practical standpoint, Fe₂AlB₂ offers several advantages as a magnetic refrigerant: it is composed entirely of earth-abundant, non-toxic, and inexpensive elements (Fe, Al, B), eliminating the supply-chain and cost concerns associated with rare-earth-based magnetocaloric materials such as Gd₅(Si₂Ge₂). However, the MCE performance of bulk Fe₂AlB₂ remains lower than those of benchmark materials such as Gd₅Si₂Ge₂.

($-\Delta S_m \approx 14\text{--}19 \text{ J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ at 2–5 T) and $\text{MnFeP}_{0.45}\text{As}_{0.55}$ ($-\Delta S_m \approx 14.5\text{--}18 \text{ J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ at 2–5 T) [99], indicating that further compositional and microstructural optimization is required. Recent efforts have explored chemical substitutions on the Fe and Al sites, such as Mn, Co, Ge, and Ga doping [13,15,225], to tune the Curie temperature and enhance the MCE, demonstrating the chemical tunability of this MAB-phase system for magnetic cooling applications.

For the RHIP Fe_2AlB_2 specimen described in Section 5.6.2, Da Igreja et al. reported a Curie temperature of 295.5 K and magnetic entropy changes of 2.9 and 6.8 $\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ at 2 and 5 T, respectively [194]. Flux-grown $(\text{Fe}_{1-x}\text{Mn}_x)_2\text{AlB}_2$ crystals also enabled composition- and direction-dependent magnetic phase-diagram studies [204], while $\text{Mo}_{4/3}\text{Ho}_{2/3}\text{AlB}_2$ was reported to order antiferromagnetically below 9 K [26].

Electromagnetic absorption provides another functional use of bulk-derived powders. Bai et al. evaluated the Joule-heated $(\text{Fe}_{1-x}\text{Mn}_x)_2\text{AlB}_2$ series as powder/paraffin mixtures at a mass ratio of 6:4 [195]. From the measured electromagnetic parameters, they reported a minimum reflection loss of -47.8 dB at 12.24 GHz and an effective bandwidth of 4.16 GHz for $(\text{Fe}_{0.3}\text{Mn}_{0.7})_2\text{AlB}_2$ at a calculated absorber thickness of 1.5 mm. These values characterize the powder/paraffin absorber and its thickness-dependent response.

WAlB exhibits intermediate transport properties, with an electrical conductivity of $1.11 \times 10^6 \text{ S}\cdot\text{m}^{-1}$ and thermal conductivity of $10.38 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ [105]. Among the *i*-MAB phases, the thermal conductivities of $\text{Mo}_{4/3}\text{Lu}_{2/3}\text{AlB}_2$ and $\text{Mo}_{4/3}\text{Y}_{2/3}\text{AlB}_2$ are further reduced to 9.90 and $11.73 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, respectively [168,170]. These

i-MAB-phase materials have chemically ordered metal sites. Their contrast with MoAlB cannot be attributed automatically to random-solute scattering; changes in crystal structure, bonding, electronic states and specimen microstructure must also be considered. The 211-type MAX-phase borides Zr₂SB and Nb₂SB exhibit thermal conductivities of 12.01 and 13.79 W·m⁻¹·K⁻¹, respectively [97,100]. Table 7 compiles total thermal conductivities; comparison with the Wiedemann–Franz relation requires separation of the electronic contribution.

A useful theory–experiment comparison therefore matches the observable before comparing its magnitude. Heat capacity requires the same mass or molar basis and the relevant vibrational, electronic and magnetic terms; expansion requires matching direction and temperature interval [99,101,121]. For conductivity, a lattice-only calculation must be compared with a separately estimated lattice contribution, whereas Table 7 compiles total experimental values. This distinction explains why agreement in heat capacity or expansion does not by itself validate a conductivity prediction.

Table 7. Reported experimental thermal expansion coefficients (α , 10⁻⁶ K⁻¹, averaged over source-specific temperature intervals) and near-room-temperature thermal conductivity (κ , W·m⁻¹·K⁻¹) and electrical conductivity (σ , 10⁶ S·m⁻¹) for selected experimentally synthesized MAB phases and related nanolaminated transition-metal borides.

Materials	Thermal Expansion Coefficient (10 ⁻⁶ K ⁻¹)	Thermal Conductivity (W·m ⁻¹ ·K ⁻¹)	Electrical Conductivity (10 ⁶ S·m ⁻¹)
MoAlB [98]	10.1	37.56	2.70
MoAlB [2]	9.5	35.0	2.04–2.86
MoAlB [103]	–	29.21	2.91
Mn ₂ AlB ₂ [95]	18.6	–	0.19–0.20
Fe ₂ AlB ₂ [4]	–	–	0.44
Fe ₂ AlB ₂ [101]	10.3	–	–

Materials	Thermal Expansion Coefficient (10^{-6} K^{-1})	Thermal Conductivity ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)	Electrical Conductivity ($10^6 \text{ S} \cdot \text{m}^{-1}$)
Fe_2AlB_2 [99]	13.5	7.5	0.374
Fe_2AlB_2 [102]	—	7.47	0.617
Cr_2AlB_2 [101]	10.5	—	—
WAlB [105]	9.15	10.38	1.11
$\text{Mo}_{4/3}\text{Lu}_{2/3}\text{AlB}_2$ [170]	8.57	9.90	1.22
$\text{Mo}_{4/3}\text{Y}_{2/3}\text{AlB}_2$ [168]	8.38	11.73	0.66
Zr_2SB [97]	7.64	12.01	1.74
Nb_2SB [100]	7.1	13.79	1.17

6.3 High-Temperature Properties

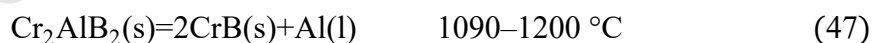
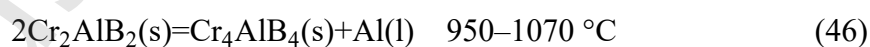
At elevated temperatures, oxidation can either protect or degrade the Al-containing MAB-phase materials considered here. Oxide composition, scale continuity and adhesion, volatility, and transport through the scale determine the balance. The following oxidation, crack-healing and ablation examples relate these surface reactions to the parent structure while retaining the different exposure conditions [201,212,226].

6.3.1 High-Temperature Oxidation Resistance

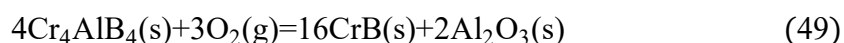
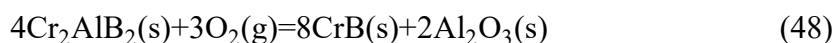
Regarding high-temperature oxidation behavior, various MAB-phase materials show significant differences. Oxidation of Cr_2AlB_2 begins at approximately 680 °C [106], but the material retains good oxidation resistance up to at least 1100 °C owing to the formation of a protective Al_2O_3 scale. As shown in Fig. 13(a), during isothermal oxidation from 700 °C to 1200 °C, the mass gain vs. time curve exhibits a characteristic two-stage behavior: at the onset of oxidation, mass increases rapidly following a linear rate law; subsequently, due to the formation of a dense oxide film on the surface, the oxidation rate drops sharply and follows a parabolic rate law. At

750 °C and below, the oxide film mainly consists of Cr₂O₃; whereas when the temperature reaches 800 °C and above, the oxide film transforms into the more stable and protective Al₂O₃. In the high-temperature range (>950 °C), Cr₂AlB₂ itself undergoes thermal decomposition. At this point, the elemental aluminum precipitated from the lattice is rapidly oxidized preferentially, forming an Al₂O₃ protective layer [106]. This process not only consumes oxygen but also effectively protects the remaining matrix (such as CrB) from further oxidation through the formed Al₂O₃ film. Thermodynamic calculations confirm that the formation of the "Al₂O₃+ CrB" combination, rather than the individual oxides of Cr and B, is the most energetically favorable pathway, which is consistent with the experimentally observed final product composition. Therefore, despite decomposition at high temperatures, Cr₂AlB₂ powder exhibits good oxidation resistance up to at least 1100 °C, owing to the continuous outer Al₂O₃ protective film. The decomposition and oxidation reactions of Cr₂AlB₂ are as follows [106]:

Thermal Decomposition Reactions (in argon atmosphere):

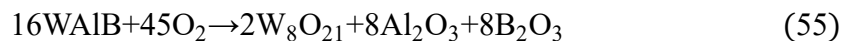
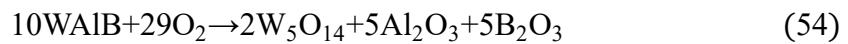
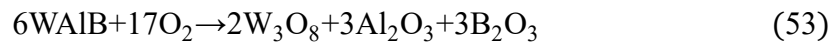
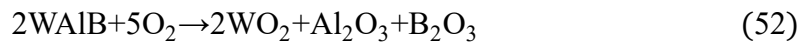
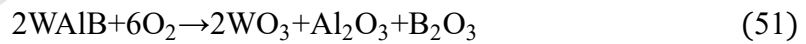


Oxidation Reactions (in air atmosphere):



In an argon inert atmosphere [174], the WAIB phase can remain stable up to

800 °C. Between 700 °C and 800 °C, WAlB begins to undergo slight degradation, with tungsten-boron binary compounds such as WB₂, W₂B, and WB₄ detected in the products. When the temperature rises above 900 °C, the degradation process intensifies, with the WB phase becoming the main product, accompanied by trace amounts of WO₃. The essence of this degradation process is a dealumination reaction: WAlB → WB + Al. As shown in Fig. 13(b), in an air atmosphere, the oxidative stability of WAlB can be maintained only up to approximately 500 °C. Starting at 500 °C, various tungsten oxides and Al₂O₃ begin to form on the sample surface; oxidation intensifies at 600 °C with cracks appearing on the sample surface; above 800 °C, the oxidation rate increases sharply, and the WAlB phase is almost completely converted to oxides. SEM observations reveal that the oxide layer formed between 400–600 °C is porous and prone to cracking, unable to provide effective protection for the underlying material, leading to continuous oxidation until complete conversion. The possible chemical reactions for the oxidation of the WAlB phase are as follows [174]:

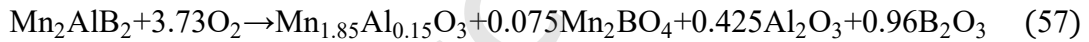


For isothermal oxidation, the time dependence of the mass gain per unit area ($\Delta W/A$) can be generally analyzed through a power-law relationship [227]:

$$\Delta W/A = k' t^n \quad (56)$$

where k' is the fitted rate constant and n is the kinetic exponent. Values near 1 and 0.5 describe linear and parabolic net mass-change kinetics, respectively, while $n < 0.5$ describes sub-parabolic behavior. A low exponent alone does not prove protection: volatilization and spallation can reduce the net mass gain, so scale continuity, thickness and phase analysis must also be examined.

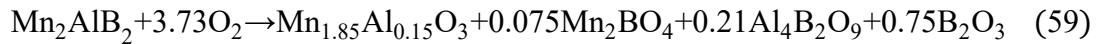
As illustrated in Fig. 13(c) (left panel), the tested Mn_2AlB_2 samples showed slow mass-gain kinetics at 700 °C ($n = 0.13$) for at least 96 h, together with a protective $\text{Mn}_{2-x}\text{Al}_x\text{O}_3$ -based scale [227]. The following simplified oxidation balance was proposed in Ref. [227] using $x \approx 0.15$; its numerical coefficients are rounded:



A more general form is:



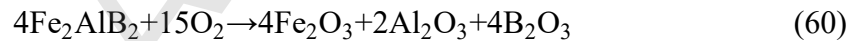
The XPS analysis of the specimen oxidized at 700 °C for 6 h supported the presence of B_2O_3 , while the Al-bearing manganese oxide was represented as $\text{Mn}_{2-x}\text{Al}_x\text{O}_3$ [227]. To describe aluminum-borate formation at higher temperatures, Ref. [227] also proposed the following schematic balance with rounded coefficients. It uses an assumed $\text{Mn}_{2-x}\text{Al}_x\text{O}_3/\text{Mn}_2\text{BO}_4$ assemblage:



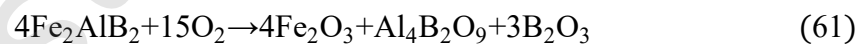
The measured phase evolution must be distinguished from this schematic balance. At 900 °C after 6 h, Mn_3O_4 was the dominant crystalline oxide detected by XRD. After 96 h at the same temperature, $\text{Al}_{18}\text{B}_4\text{O}_{33}$ became the predominant oxide, with

Mn₃O₄ still present [227]. Oxide-scale spallation occurred at 800–900 °C and was severe at 900 °C, limiting oxidation resistance under those exposure conditions [227].

As shown in Fig. 13(c) (right panel), Fe₂AlB₂ exhibits a two-stage oxidation behavior in air at 900 °C [227]. Within the first 60 hours, the oxidation rate is relatively fast ($n \approx 0.85$). After 60 hours, the kinetics shift to a sub-parabolic pattern ($n = 0.42\text{--}0.46$), and the oxidation rate decreases significantly. This transition is attributed to the formation of a passivating layer with excellent adhesion. As revealed in the cross-sectional SEM micrograph shown in Fig. 13(d), this passivating layer maintains intimate contact with the substrate even at corners without any sign of spallation [227]. XPS analysis indicates that this passivating layer is Al₄B₂O₉, rather than Al₂O₃. During the initial stage of oxidation, Al₂O₃ and Fe₂O₃ are formed [227]. A simplified oxidation reaction is:

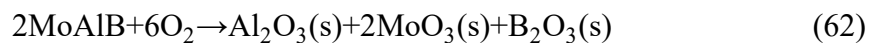


At 1000 °C, Al₂O₃ and B₂O₃ react to form Al₄B₂O₉:



At 900 °C and above, B₂O₃ is presumed to evaporate. At both 800 °C and 1000 °C, however, oxidation is rapid and severe, and an effective protective layer does not form [227].

At high temperatures in air, the oxidation of MoAlB is a complex process, primarily forming MoO₃, Al₂O₃, and B₂O₃ [228]. The initial overall oxidation reaction is:



When the temperature exceeds 800 °C, the Al_2O_3 formed reacts with B_2O_3 to produce the more stable compound $\text{Al}_4\text{B}_2\text{O}_9$ (i.e., $2\text{Al}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$). At 1100 °C, the initial mass gain of porous MoAlB is followed by a decrease in sample mass [228]. As shown in Fig. 13(e), at 1000 °C and below, the oxidation process of porous MoAlB can be generally divided into three stages: the oxide film formation period, the oxidation saturation period, and the oxidation stabilization period. During the stabilization period (e.g., at 1000 °C), the square of the mass gain per unit area shows a linear relationship with time. The observed Al-rich protective scale provides direct evidence of selective oxidation [228]. Thermodynamic comparisons depend on temperature and oxygen potential, with reaction energies normalized to a common oxygen basis. Scale growth also depends on transport of Al and oxygen through the evolving reaction layer. Despite the volatilization of MoO_3 and B_2O_3 , porous MoAlB still exhibits good oxidation resistance during long-term oxidation at 1000 °C and below, primarily attributed to the protective oxide layer which is predominantly composed of Al_2O_3 . However, at 1100 °C, the volatilization rate of MoO_3 increases sharply, creating new pores in the oxide layer that allow more oxygen ingress, intensifying internal oxidation and leading to significant deterioration in oxidation resistance.

Shi et al. [229] studied the high-temperature oxidation of MoAlB single crystals and found that oxidation initiates around 720 °C, with sample weight reaching its maximum at 1100 °C; the weight loss above 1100 °C is attributed to MoO_3 evaporation due to its high vapor pressure. As shown in Fig. 13(f), the oxidation

process of MoAlB single crystals is notably anisotropic: compared to the (100) and (001) crystal planes, the (010) plane exhibits better oxidation resistance. In the orthorhombic MoAlB structure (space group *Cmcm*), the Al atomic bilayers lie parallel to the (010) plane; this geometry is consistent with an orientation-dependent supply of Al to the growing scale. The solid solution of Si can significantly enhance the high-temperature oxidation resistance of MoAlB [230]. As shown in Fig. 13(g), after oxidation in air at 1200–1400 °C for 10 hours, the MoAl_{0.97}Si_{0.03}B solid solution exhibits lower mass gain and thinner oxide scale compared to undoped MoAlB, indicating a slower oxidation rate. The improvement in oxidation resistance is mainly attributed to two factors. First, similar to MoAlB, a dense and continuous Al₂O₃ oxide layer forms on its surface, serving as the primary protective barrier. Second, and more critically, the solid-solved Si generates a SiO₂ glass phase during oxidation. Above 1200 °C, this glassy phase becomes fluid and can partially fill pores created by the evaporation of volatile oxides MoO₃ and B₂O₃, thereby effectively hindering inward oxygen diffusion and slowing the oxidation rate. Therefore, Si solid solution enhances the material's oxidation resistance synergistically with the Al₂O₃ layer by forming a flowable SiO₂ glass phase that seals the diffusion pathways within the oxide scale. Si addition and SiC reinforcement also reduced oxide-scale growth in SPS-processed MoAlB [231]. In contrast, the (Mo,W)AlB, (Mo,Cr)AlB and (Mo,W,Cr)AlB specimens in Ref. [5] did not show a comparable oxidation improvement under their reported conditions. Scale growth, adhesion and protective performance depend on the substitution and exposure conditions.

The good oxidation resistance of MAB phases can also be exploited in practical applications. For instance, the MoAlB phase can be incorporated as a secondary phase into ultra-high temperature ceramics to enhance their oxidation resistance [232]. As shown in Fig. 13(h), incorporating an appropriate amount of the MoAlB MAB phase into ZrB₂-SiC composites can significantly enhance their oxidation resistance in air at 1600 °C, evidenced by a notable reduction in oxide layer thickness (from 250 μm to 108 μm) [232]. The underlying mechanism lies in the fact that the Al₂O₃ formed by the oxidation of MoAlB alters the composition of the glass phase in the oxide layer, transforming it from B₂O₃-SiO₂ to SiO₂-Al₂O₃, and simultaneously reduces the viscosity of this glass phase. The moderate viscosity endows the glass phase with favorable fluidity, enabling it to effectively cover and fill surface pores, thereby forming a denser protective layer [232].

The connection to Section 3.2 is thus chemical as well as mechanical: the Al-bearing regions of conventional MAB structures provide an Al reservoir, while the M-B/B-B framework contributes to the remaining substrate. Selective oxidation can create a protective layer only when its growth and adhesion outweigh volatilization, cracking and Al depletion. Bond anisotropy helps identify plausible transport or separation pathways, but the contrasting Cr-, Fe-, Mn- and Mo-based oxide scales show why weak A-related bonding is not a sufficient predictor of oxidation resistance.

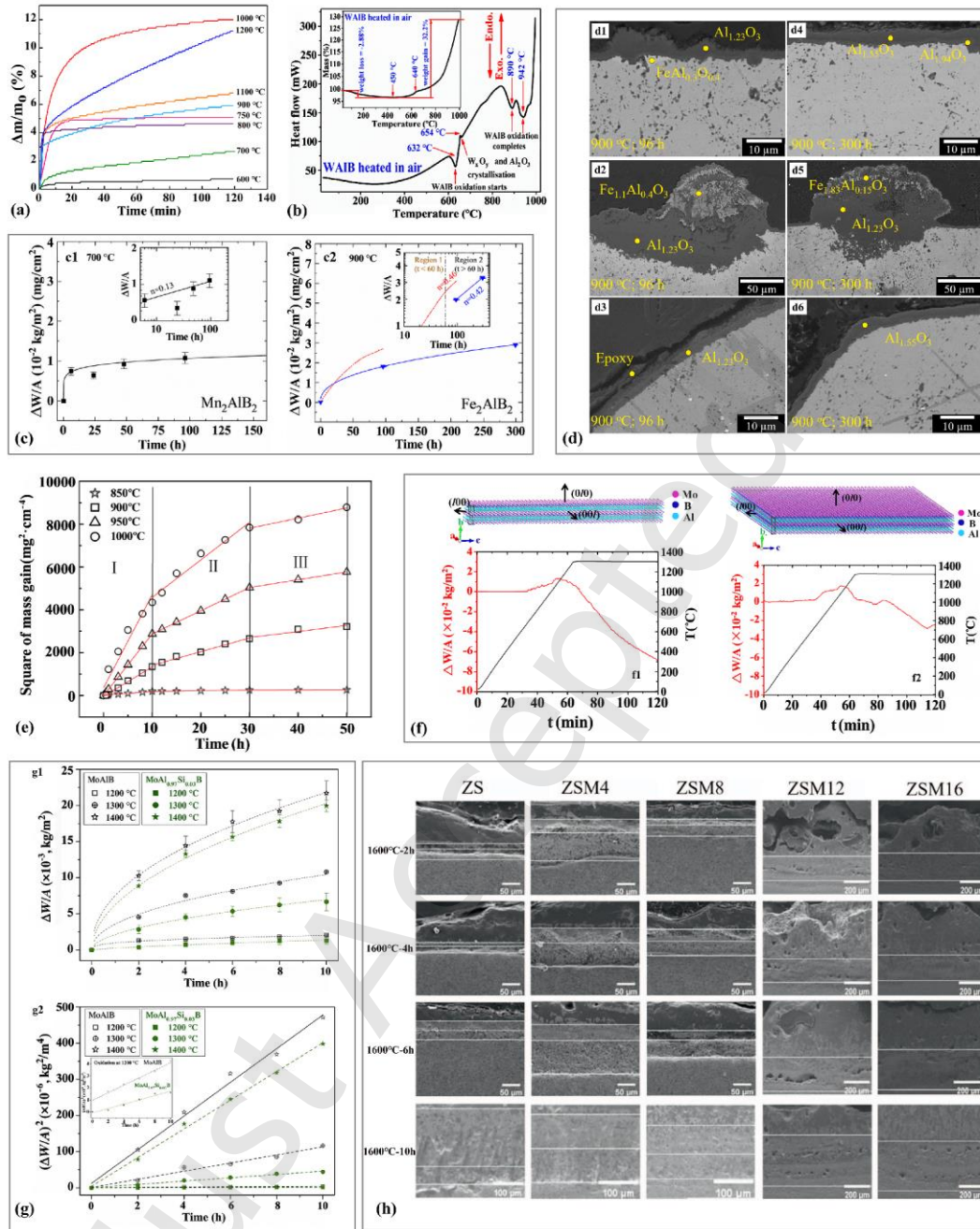


Fig. 13. Oxidation measurements and microstructures: (a) Cr_2AlB_2 powder [106]; (b) WAIB [174]; (c,d) $\text{Mn}_2\text{AlB}_2/\text{Fe}_2\text{AlB}_2$ kinetics and Fe_2AlB_2 scale sections [227]; (e) porous MoAlB [228]; (f) oriented MoAlB crystals [229]; (g) MoAlB and Si-substituted MoAlB [230]; (h) MoAlB-containing ZrB₂-SiC composites [232]. Exposure conditions are specified in Section 6.3.1. Adapted with permission from Ref. [106] for (a), © Elsevier Ltd 2020; Ref. [174] for (b), © Elsevier Ltd 2024; Ref. [227] for (c,d), © Elsevier Ltd 2024; Ref. [228] for (e), © Elsevier Ltd and Techna Group S.r.l. 2023; Ref. [229] for (f), © Elsevier Ltd and Techna Group S.r.l. 2018; Ref. [230] for (g), © Elsevier Ltd 2019. Adapted from Ref. [232] (<https://doi.org/10.1088/2053-1591/ad1f9b>) for (h), © The Author(s) 2024, published by IOP Publishing Ltd, under CC BY 4.0 (<https://creativecommons.org/licenses/by/4.0/>); panel rearranged.

6.3.2 High-Temperature Self-Healing Performance

Oxidation-assisted crack healing has been experimentally demonstrated in MoAlB [7], alongside the oxidation and thermal-shock behavior discussed in Refs. [2,213]. In the test reproduced in Fig. 14(a–e), water-quench damage reduced the flexural strength from about 306.8 to 136.4 MPa. After 4 h in air at 1200 °C, the reported strength was about 293.9 MPa: approximately 96% of the initial value. Microscopy and phase analysis identified Al₂O₃ as the crack-filling product [7].

The mechanism connects the Al-bearing parent to the damaged region: access of oxygen to crack surfaces allows oxidation products to grow into the available gap, while volatilization of Mo- and B-containing oxides changes the retained product assemblage (Fig. 14(c–e)). Retention of an adherent alumina filling can restore load transfer across the crack. The relatively close thermal expansions of MoAlB and alumina may reduce cooling mismatch; the residual-stress state requires direct measurement.

Oxidation-assisted healing is also reported for MAX ceramics, including Ti₂AlC and Cr₂AlC [107,108]. Healing rates and strength recovery depend on crack dimensions, exposure time, temperature and atmosphere [3,7]. In MoAlB, healing competes with substrate consumption and scale damage.

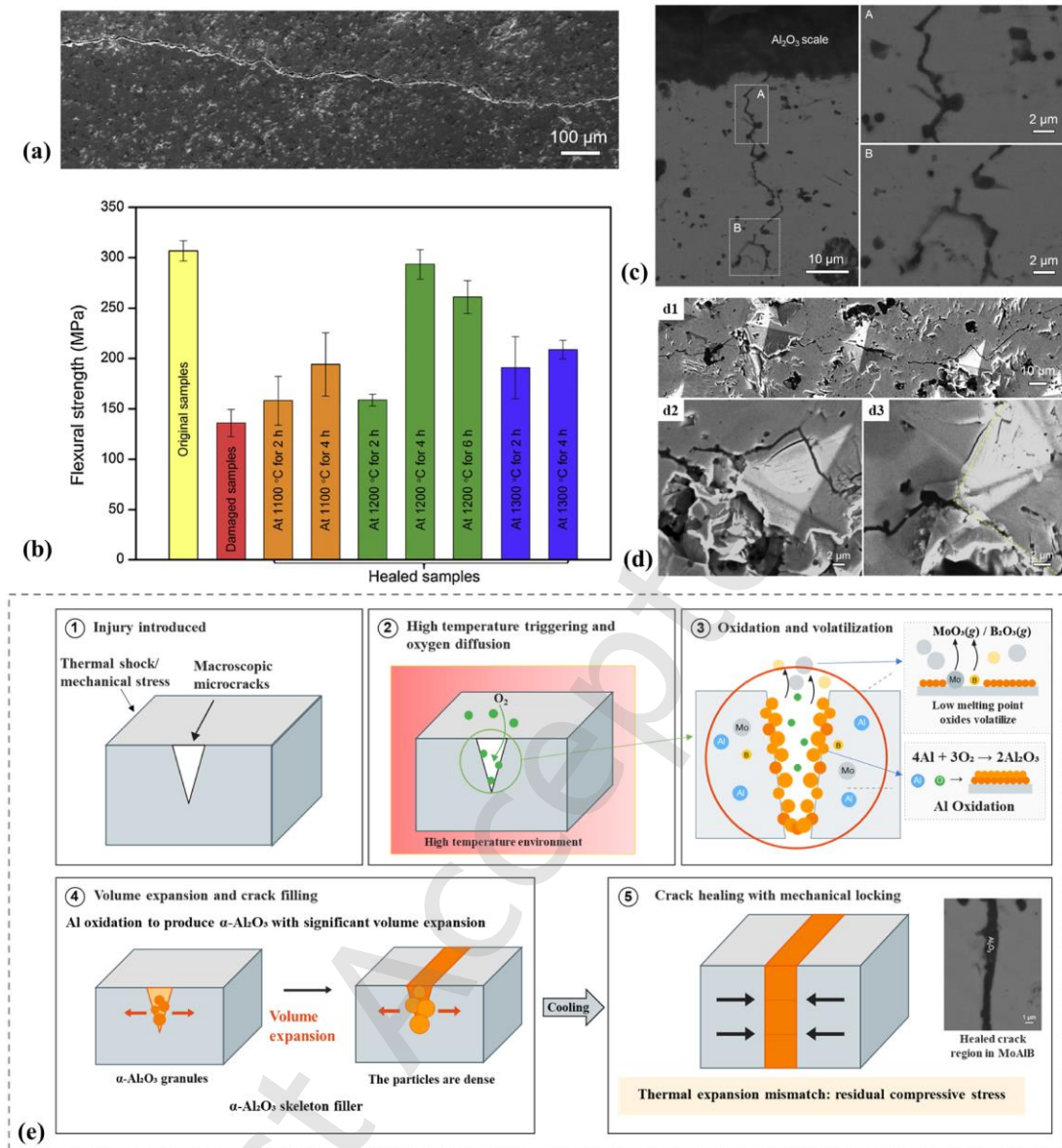


Fig. 14. Oxidation-assisted crack healing in MoAlB: (a) thermal-shock crack, (b) measured flexural-strength recovery, (c,d) crack-filling alumina and local microscopy, and (e) a proposed mechanism [7]. Mechanistic interpretation is discussed in Section 6.3.2. Adapted with permission from Ref. [7], © Elsevier Ltd 2019.

6.3.3 Ablation Resistance

Bei et al. [226] systematically studied the ablation behavior of dense MoAlB ceramic prepared by SPS sintering under an oxyacetylene flame (flame temperature was around 3000 °C). As shown in Fig. 15(a), during the initial ablation stage (within 60 seconds), a viscous, protective Al_2O_3 oxide layer rapidly formed on the surface of

MoAlB ceramic, reducing its linear ablation rate from 1.3 $\mu\text{m/s}$ in the first 30 seconds to $-0.7 \mu\text{m/s}$ after 60 seconds, demonstrating excellent short-term ablation resistance. However, as the ablation time extended to 120 seconds and beyond, this Al_2O_3 protective layer became porous, damaged, and eventually failed, as reflected by the surface appearance evolution in Fig. 15(b), due to erosion by high-speed gas flow and continuous high-temperature chemical reactions. They concluded that the ablation resistance of MoAlB highly depends on the formation and maintenance of the surface Al_2O_3 protective layer, and its failure results from the combined effects of thermochemical oxidation and physical-mechanical erosion.

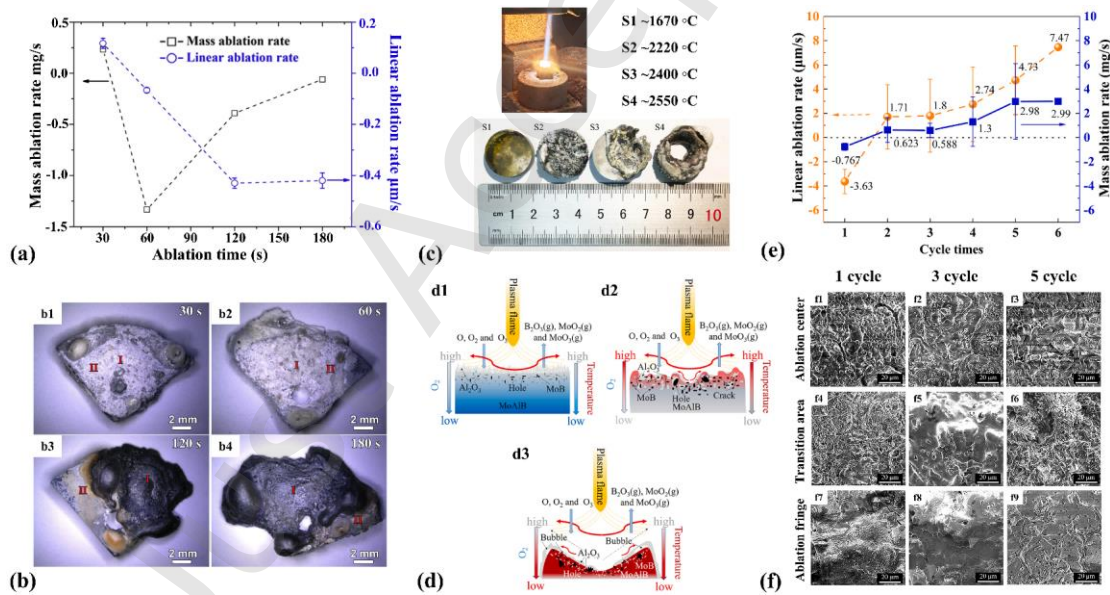


Fig. 15. MoAlB ablation under three exposure protocols: (a,b) rates and surface appearance during oxyacetylene-flame testing [226]; (c,d) surfaces and proposed mechanisms during air-plasma exposure [201]; (e,f) cyclic rates and center/transition/edge microstructures under nitrogen plasma [212]. Exposure conditions and interpretations are given in Section 6.3.3. Adapted with permission from Ref. [226] for (a,b), © Elsevier Ltd 2019; Ref. [201] for (c,d), © Elsevier Ltd 2021; Ref. [212] for (e,f), © Elsevier Ltd 2024.

Su et al. [201] systematically investigated the ultra-high-temperature ablation behavior of bulk MoAlB ceramic prepared by SPS, exposing it to an air plasma flame

at temperatures ranging from approximately 1670 °C to 2550 °C for about 30 seconds. The ablated samples at each temperature are shown in Fig. 15(c). They found that the linear ablation rate increased sharply from 0 $\mu\text{m/s}$ at 1670 °C to 86.4 $\mu\text{m/s}$ at 2550 °C. The ablation mechanisms across these temperature regimes are summarized in Fig. 15(d): at lower temperatures (~ 1670 °C), a protective Al_2O_3 oxide layer formed on the material surface, leading to excellent ablation resistance; when the temperature was raised to ~ 2220 °C, macrocracks induced by thermal stress provided channels for inward oxygen diffusion, aggravating substrate ablation; at temperatures above ~ 2400 °C, the formation of volatile oxides (such as MoO_3 and B_2O_3) and mechanical erosion of the viscous oxide layer by high-speed plasma flow became the dominant ablation mechanisms.

Zhang et al. [212] further investigated the cyclic ablation behavior and mechanisms of MAB-phase MoAlB ceramic under a nitrogen plasma flame at approximately 2000 °C, aiming to evaluate its applicability limits as a reusable thermal protection material. As shown in Fig. 15(e), MoAlB ceramic prepared by SPS maintained structural integrity after up to 5 cycles (5 minutes per cycle, totaling 25 minutes) of ablation, with linear and mass ablation rates of 4.73 $\mu\text{m/s}$ and 2.98 mg/s , respectively. The SEM images of the ablated surface regions across different cycle stages, shown in Fig. 15(f), reveal the progressive microstructural evolution underlying the three-stage dynamic ablation model proposed by the researchers. In the initial stage of ablation, Al elements from the matrix diffuse outward and react with oxygen, in-situ forming a multiphase oxidation-resistant barrier on the material

surface composed of dense Al_2O_3 and refractory MoB and Mo_2B phases. This barrier effectively blocks the inward penetration of heat and oxygen. However, as thermal cycling proceeds, under the coupled action of high-speed scouring by the high-temperature plasma and periodic thermal stress, the surface oxide film gradually undergoes mechanical spallation and structural degradation, exposing fresh matrix and triggering rapid oxidation and decomposition. Therefore, the cyclic failure of MoAlB is a typical thermo-mechanical-chemical coupled process. The main loss mechanisms include surface oxidation, phase decomposition, and mechanical erosion induced by the gas flow. The middle stage of the proposed model, corresponding to cycles 3–4, is illustrated in Fig. 11(c).

The ablation behavior of MoAlB contrasts instructively with that of ZrB_2 -based ceramics, the benchmark UHTCs for thermal protection. For monolithic ZrB_2 , oxidation protection at temperatures below $\sim 1100^\circ\text{C}$ is provided by a continuous B_2O_3 glassy layer formed on top of an underlying ZrO_2 scale; however, above $\sim 1100^\circ\text{C}$ the protective B_2O_3 rapidly evaporates due to its high vapor pressure, leaving only a porous ZrO_2 scale that fails to shield the substrate from further oxygen ingress [233–235]. This intrinsic limitation of pure ZrB_2 at ultra-high temperatures has motivated the incorporation of SiC to form ZrB_2 -SiC composites, in which a ZrO_2 - SiO_2 composite oxide layer is established for high-temperature protection. Nevertheless, the structural stability of this oxide layer is still progressively compromised under multi-cycle and long-duration ablation by the violent evaporation of the SiO_2 glassy phase together with the aggregation and grain growth of ZrO_2 ,

which collectively destabilize the protective scale and limit the reusability of ZrB₂-SiC systems under cyclic plasma exposure [236,237]. For MoAlB, the Al reservoir can support regeneration of an alumina-rich surface, but protection remains limited by oxidation consumption, scale melting or removal and the imposed heat flux. The bulk-material and composite observations in Refs. [212,232] therefore require comparisons at matched heat flux, gas chemistry, duration, cycling and erosion conditions.

6.4 Friction and Wear-Resistant Materials

The tribological response of the experimentally studied Al-containing MAB ceramics couples bulk load support with surface chemistry [158,162,238 – 240]. The relatively stiff M–B/B–B framework discussed in Sections 3.2 and 4.2.2 can contribute to indentation resistance, while easier shear or separation along particular A-related regions may affect local damage. During sliding of MoAlB, Al, B and Mo can supply Al₂O₃, B₂O₃ and MoO₃, respectively; the retained tribofilm also depends on temperature, oxygen supply and material transferred from the counterpart. Thermal transport affects contact heating, but the conductivities in Table 7 vary substantially among compositions.

The friction coefficients of MAB phases display a pronounced dependence on temperature, counterpart material, and applied load, with the overall trends summarized in Fig. 16. As shown in Fig. 16(a), when Fe₂AlB₂ slides against GCr15 steel, the friction coefficient decreases markedly with increasing sliding speed, falling into the range of 0.3–0.4 above 3.2 m/s and reaching as low as ~0.3 at 6.4 m/s [238].

The load dependence of the friction coefficient is strongly influenced by counterpart hardness: for MoAlB sliding against Al₂O₃ at room temperature, the friction coefficient increases from 0.36 to 0.89 as the normal load rises from 1 N to 10 N, whereas against the softer 100Cr6 steel counterpart, it decreases from 0.89 to 0.77 over the same load range [240]. At intermediate-to-high temperatures (Fig. 16(c)), wear-track analyses of the MoAlB/Inconel 718 tribopair reveal that the friction coefficient reaches a maximum of 0.79 at 200 °C, decreases to 0.53 at 600 °C when optimal tribological performance is achieved, and further drops to 0.36 at 800 °C, despite aggravated wear caused by partial peeling of the tribofilm [158]. The most striking performance is observed in the ultra-high-temperature regime (Fig. 16(b)): at 1200 °C, the friction coefficient of MoAlB against Al₂O₃ drops as low as ~0.32, while that against Si₃N₄ also decreases substantially to ~0.5, both representing marked reductions compared with the elevated values recorded at 800–1000 °C [239]. These observations identify useful operating windows rather than a monotonic family-wide trend. In particular, the lower friction at 800 °C for MoAlB/Inconel 718 accompanies increased wear, showing that a low friction coefficient is not sufficient evidence of improved wear resistance.

In terms of wear rate, MAB phases exhibit outstanding anti-wear capability under appropriate sliding conditions. The wear of MoAlB sliding against 100Cr6 steel under 1–10 N at room temperature is extremely low [240]. At elevated temperatures, the wear rate of MoAlB against Inconel 718 reaches as low as $9.37 \times 10^{-7} \text{ mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$ at 600 °C (Fig. 16(c)) [158], and is of the order of $10^{-6} \text{ mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$

against Si_3N_4 at 800–1200 °C; against Al_2O_3 , it reaches $3.75 \times 10^{-5} \text{ mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$ at 1000 °C (Fig. 16(b)) [239]. Under other sliding conditions, the wear rate is substantially higher; for example, the wear rate of MoAlB sliding against Al_2O_3 under 10 N at room temperature reaches $5.24 \times 10^{-4} \text{ mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$ [240], while Mn_2AlB_2 sliding against WC, Al_2O_3 and Si_3N_4 shows friction coefficients as high as 0.72–0.87 and wear rates on the order of $10^{-3} \text{ mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$, with the response depending on the counterface material and sliding conditions (Fig. 16(d)) [162]. The wear rate of Fe_2AlB_2 falls within $(0.5\text{--}2.5) \times 10^{-5} \text{ mm}^3 \cdot \text{N}^{-1} \cdot \text{m}^{-1}$ [238].

Wear-track observations in selected MoAlB tests identify the evolving tribofilm as an important control on steady-state friction and wear [158]. Substrate fracture and deformation also contribute, with their relative importance depending on the material and sliding conditions. When sliding against steel, a "third-body" transfer layer or tribofilm forms on the worn surface, composed of metallic oxides (e.g., Fe and Cr oxides) transferred from the counterpart and self-oxidation products of the MAB phase (e.g., B_2O_3 and MoO_3), exhibiting characteristic rippled morphologies (Fig. 16(e)) [240]. For instance, the tribofilm rich in Ni, Cr and Fe oxides formed on the MoAlB/Inconel 718 tribopair at elevated temperatures provides effective lubrication [158], while the mixed iron–manganese oxide layer formed on the Mn_2AlB_2 /100Cr6 tribopair under mild conditions effectively protects the substrate [162]. At ultra-high temperatures (e.g., 1200 °C), a dense nanocrystalline Al_2O_3 tribofilm ($\sim 5 \mu\text{m}$ thick, grain size $\sim 200 \text{ nm}$, accompanied by pronounced dislocation-mediated plastic deformation, Fig. 16(f)) develops on the MoAlB worn surface through outward

diffusion and in situ oxidation of Al from the MoAlB matrix; the high-temperature plastic deformability of this layer, acting synergistically with the discontinuous MoO₃ lubricating film, results in extremely low friction and wear [239]. The transition of wear mechanisms is governed by the stability of this surface film: when the film remains continuous and dense, mild oxidative wear and adhesion prevail; when the particular load, speed and temperature destabilize the film, leading to film rupture or microfracture of the underlying material, the dominant wear mode transitions to severe abrasive wear, adhesive wear, and fatigue spalling [158,162,238].

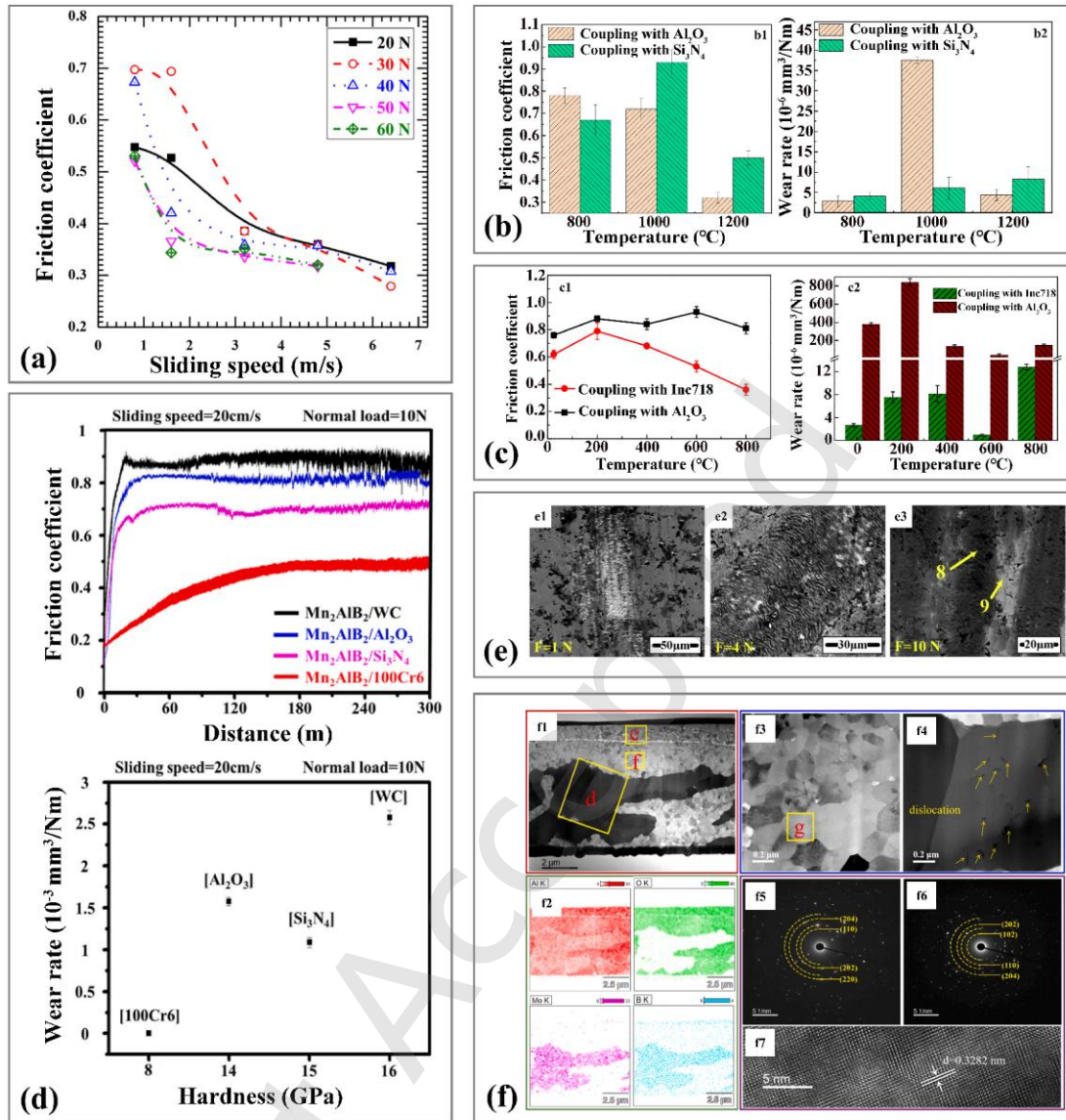


Fig. 16. Tribological measurements and worn-surface characterization: (a) $\text{Fe}_2\text{AlB}_2/\text{GCr15}$ [238]; (b) $\text{MoAlB}/\text{Al}_2\text{O}_3$ or Si_3N_4 [239]; (c) $\text{MoAlB}/\text{Al}_2\text{O}_3$ or Inconel 718 [158]; (d) Mn_2AlB_2 with different counterfaces [162]; (e) $\text{MoAlB}/100\text{Cr6}$ tribofilm [240]; and (f) microscopy, diffraction and elemental analysis of the $\text{MoAlB}/\text{Al}_2\text{O}_3$ wear track at 1200 °C [239]. Conditions and the distinction between friction and wear are discussed in Section 6.4. Adapted with permission from Ref. [238] for (a), © Elsevier Ltd and Techna Group S.r.l. 2020; Ref. [239] for (b,f), © Elsevier Ltd 2023; Ref. [158] for (c), © Elsevier Ltd and Techna Group S.r.l. 2020; Ref. [162] for (d), © Elsevier B.V. 2021; Ref. [240] for (e), © Elsevier Ltd 2018.

6.5 Radiation-Resistant Materials

Radiation response depends on defect production, migration and recombination as well as cracking and phase change [8,9,109 – 111,211,241]. In Ref. [9], MoAlB

vacancy formation energies depend on the chosen chemical potentials: 0.56–0.76 eV for V_B , 1.00–1.12 eV for V_{Al} and 1.94–2.26 eV for V_{Mo} ; Al interstitials have formation energies of 6.42–6.54 eV. Mo interstitials relax into Mo_{Al} antisites and Al interstitials. The high minimum V_{Mo} migration barrier of 5.27 eV impedes removal of Mo_{Al} , whereas the 0.25 eV Al-interstitial migration barrier in Fe_2AlB_2 supports recombination pathways. This defect-specific picture is consistent with the greater amorphization resistance of Fe_2AlB_2 under the matched 150 and 300 °C tests (Fig. 17(a)). The Fe-interstitial formation energies of 4.86–5.36 eV in Ref. [9] refer to an isolated interstitial rather than an antisite pair.

This example links local structure to radiation response more directly than a single weak-bond descriptor. Al-containing regions can accommodate interstitial configurations, but the relevant migration paths, antisite-removal reactions and recombination barriers differ between $MoAlB$ and Fe_2AlB_2 [9]. Radiation tolerance therefore depends on the available defect-recombination pathways as well as the bonding architecture.

Fe_2AlB_2 demonstrates radiation-induced amorphization tolerance at 150 °C and 300 °C comparable to CVD-SiC, exhibiting similar amorphization behavior under identical conditions [9]. Typical MAX phases like Ti_3SiC_2 and Ti_2AlC show higher amorphization resistance, remaining crystalline under high-dose irradiation at 150 °C; the MAX specimens developed cracking in the matched tests of Ref. [9], whereas cracking was not observed in the tested $MoAlB$, Fe_2AlB_2 and SiC specimens (Fig. 17(b)). This distinction separates retention of crystallinity from resistance to cracking.

Regarding the amorphization threshold, Fe_2AlB_2 undergoes amorphization at a dose of 0.4 dpa under room-temperature helium ion irradiation, behaving similarly to CVD-SiC [111]. Similarly, 222-type MoAlB , WAlB , and $\text{Mo}_{0.75}\text{W}_{0.25}\text{AlB}$ exhibit low room-temperature amorphization resistance, with amorphization occurring in the sub-dpa to near-dpa range, markedly below the tolerance of typical MAX phases [109,110,241]. Notably, MAB phases in the Cr-Al-B system exhibit structure-dependent radiation tolerance [8]. As shown in Fig. 17(c), Cr_3AlB_4 with a single boron ring structure retains crystallinity under irradiation at 150 °C (0.5 dpa) and 300 °C (1.0 dpa). Its reported amorphization resistance is below that of CrB but above that of Cr_3B_4 at 150 °C/0.5 dpa, and above both binary borides at 300 °C/1.0 dpa. This is attributed to the combined influence of the boron network type and the aluminum layers on defect dynamics [8].

Helium retention and bubbles add another dimension to radiation performance (Fig. 17(d)). For Fe_2AlB_2 , Ref. [111] reports an amorphous layer after room-temperature irradiation; subsequent annealing at 400 °C retained that layer, whereas annealing at 800 °C produced recrystallization and bubble growth. Irradiation at 400 °C at the same fluence produced bubbles without an amorphous layer. At 700 °C, faceted bubbles and defect structures near grain boundaries were observed. These outcomes distinguish simultaneous irradiation and thermally activated recovery from annealing a previously damaged specimen.

Cracking, volumetric swelling and retained strength are distinct measures of irradiation damage. Boron-containing compositions warrant neutron-absorption

studies, while attenuation by high-Z constituents is a separate shielding consideration; relevant spectra, isotopic composition, thickness and gas-production effects must be specified. Nuclear suitability requires coupled measurements of irradiation damage, thermophysical properties and mechanical retention under the proposed service conditions [9,110,111,211].

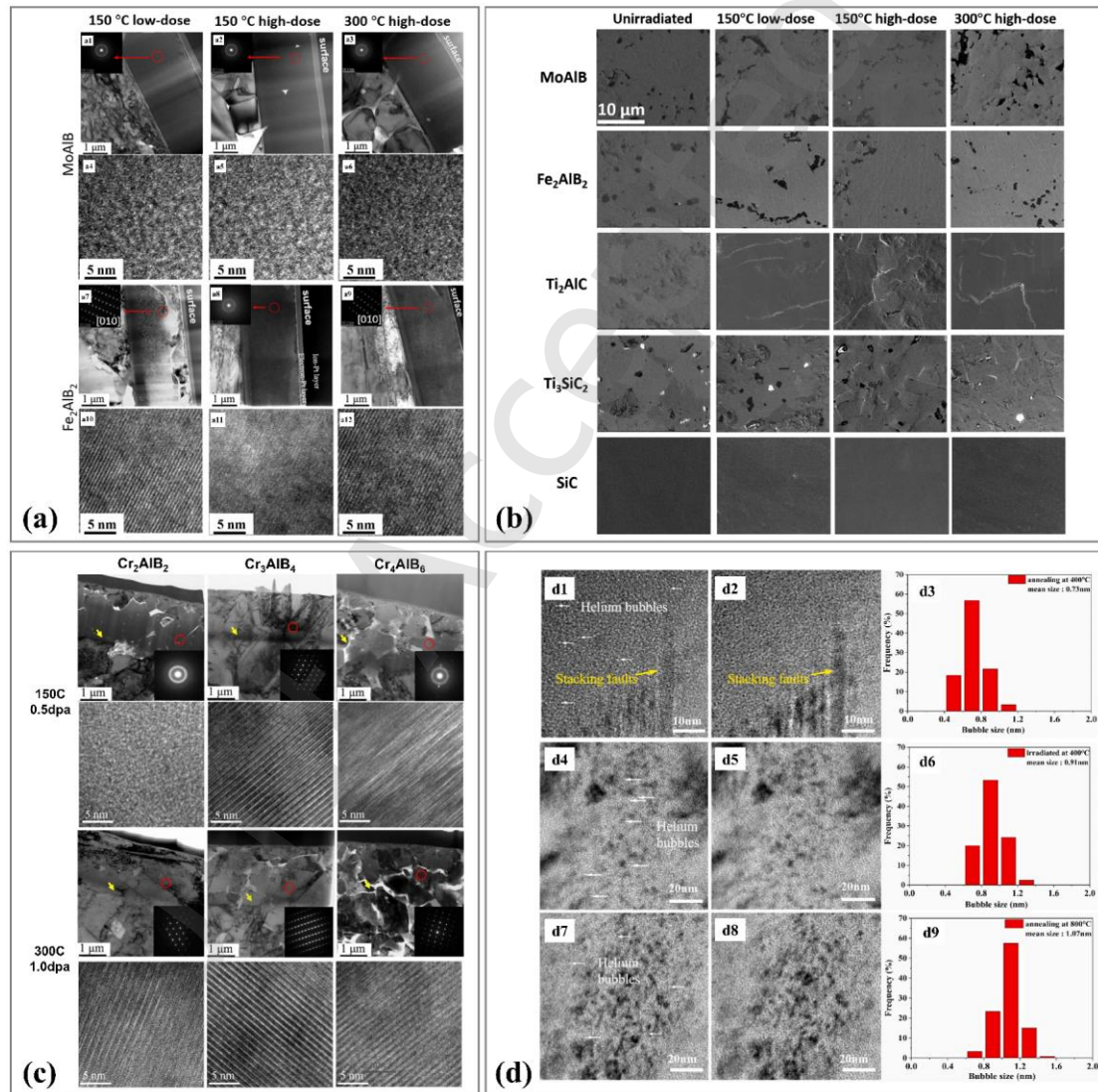


Fig. 17. Irradiation response under the conditions identified in Section 6.5: (a,b) amorphization and surface cracking in MAB-phase materials and references [9]; (c) Cr–Al–B boride microstructures [8]; (d) helium bubbles in Fe₂AlB₂ after irradiation or post-irradiation annealing [111]. Adapted with permission from Ref. [9] for (a,b), © Acta Materialia Inc. 2020, and Ref. [8] for (c), © Acta Materialia Inc. 2022, both published by Elsevier Ltd; Ref. [111] for (d), © Elsevier B.V. 2024.

6.6 From MAB Phases to MBenes: A Brief Overview of Functional Applications

The MAB–MBene connection depends on the specific transformation described in Section 5.9: an identified parent undergoes partial etching, selective removal or reconstruction, producing a material with a particular residual composition, thickness and surface chemistry [10,11,21,36]. These changes can expose adsorption sites and alter transport, but the resulting functional response belongs to the characterized product and device. The following overview distinguishes bulk electrodes, etched products, supported catalysts and devices from modeled monolayers.

Supplementary Table S2 summarizes selected energy-storage, HER and sensing results, distinguishing computational predictions from experimental electrodes, supported catalysts and sensor devices. It records the material identity, testing conditions and normalization used for each reported metric.

6.6.1 Distinctive Properties of MBenes

Boron-containing frameworks offer bonding and electronic structures distinct from carbide/nitride frameworks, including composition-dependent multicenter bonding [35,53,214]. These differences motivate composition-specific comparisons of MBenes and MXenes. Etching competes with framework dissolution and reconstruction, while terminations and residual species alter adsorption and charge transport. The parent-specific examples in Section 5.9 provide the relevant experimental context.

Four considerations connect the identified structures to their proposed or measured functions:

(1) Electrochemical response: partial Al removal, accessible surfaces and termination chemistry can change storage or catalytic behavior. The $\text{MoAl}_{1-x}\text{B}$ and MoB experiments discussed below illustrate these effects [16,45,205]. Comparisons require the same electrolyte, loading, mass or area basis, voltage window and current/scan rate.

(2) Stability: Helmer et al. combined calculations and experiments on terminated boridene, relating surface composition to structure and HER behavior [17]. Humidity-dependent sensor response in multilayer MoBT_x [56] is a device observable, distinct from chemical degradation. Comparisons with MXenes require specified composition, terminations, pH, potential, humidity, exposure duration and a common stability measurement.

(3) Mechanical response: calculated elastic properties of selected hexagonal MBene monolayers characterize the modeled structures [242]. They are not experimental strengths of etched films or evidence of long-term device fatigue resistance. Layer thickness conventions, defects, terminations and film assembly must be considered before comparing calculated moduli with bulk measurements or flexible-device performance.

(4) Structural diversity: parent symmetry and chemical ordering provide multiple starting structures, but the derivative need not preserve the parent framework [3,21,243]. Ordered-vacancy boridene [11] and bimetallic $\text{Mo}_2\text{ErB}_3\text{T}_{2.5}$ [28] illustrate different outcomes. Structural diversity motivates composition-specific design.

6.6.2 Secondary Batteries: From High-Capacity Anodes to Catalytic Hosts

(1) Lithium-ion and sodium-ion batteries

Theoretical studies evaluate specified MBene monolayers as candidate anodes for lithium-ion batteries (LIBs) and sodium-ion batteries (SIBs), using adsorption energies, diffusion barriers, storage configurations and calculated voltages [35,244–246]. These descriptors guide candidate selection for subsequent cell testing. For example, density functional theory (DFT) calculations by Bo et al. predicted that the Ti_2B_2 monolayer possesses theoretical specific capacities of 456 mAh g^{-1} (LIBs) and 342 mAh g^{-1} (SIBs), with remarkably low diffusion barriers of 0.017 and 0.008 eV, respectively [244]. Gao et al. reported that Y_2B_2 exhibits theoretical Li/Na capacities of 806 and 403 mAh g^{-1} , respectively [245], while Li et al. identified V-based MBenes, especially S-terminated V_4B_6 , as promising anode candidates owing to their low diffusion barrier and low open-circuit voltage [48]. Together with the high capacities predicted for monolayer MBenes [247], these studies suggest that MBenes can offer competitive theoretical capacities and ion-transport kinetics compared with established anode materials such as graphite, phosphorene, and Ti_3C_2 MXene [245–247].

The predicted capacity of 480 mAh g^{-1} for Li/Na storage applies to a modeled TiB monolayer [21], whereas vacuum dealloying yielded an impurity-containing layered TiB product. For molten-salt-derived HfBO, the experimental discharge capacity increased from approximately 220 mAh g^{-1} initially to approximately 420 mAh g^{-1} after 500 cycles at 0.1 A g^{-1} [84]. The tested product contained

approximately 20% HfO_2 , which the study identified as electrochemically inactive for Li storage.

Xiong et al. prepared MoB MBene from MoAlB via a fluorine-free alkaline etching method and demonstrated that, whereas pristine MoAlB is electrochemically nearly inactive, the etched MoB MBene delivered a reversible specific capacity of 671.6 mAh g^{-1} after 50 cycles at 50 mA g^{-1} in LIBs [45]. The same material retained 144.2 mAh g^{-1} after 1000 cycles at a high current density of 2 A g^{-1} . Using a molten-salt approach, Chen et al. obtained layered Mo_xB_y that maintained 638.2 mAh g^{-1} after 100 cycles at 0.1 A g^{-1} [49]. For sodium-ion storage, a microwave-assisted hydrothermal synthesis yielded MoB MBene anodes that delivered 138.6 mAh g^{-1} after 500 cycles at 500 mA g^{-1} [46]. Electrochemical impedance and scan-rate analyses in these reports help assess transport and the partition between surface-controlled and diffusion-dependent storage; such fitted contributions depend on the electrode and analysis conditions [45,49]. In a separate bulk-parent example, Shen et al. investigated defect-engineered Ti_2InB_2 as a LIB anode [37].

(2) Lithium–sulfur batteries

In lithium-sulfur (Li–S) systems, MBenes function primarily as catalytic hosts rather than as active anode materials. DFT calculations have revealed that surface Mo atoms of MoB MBene can form strong Mo–S bonds with lithium polysulfides (LiPSs), effectively immobilizing them and inhibiting the shuttle effect, while simultaneously lowering the energy barriers for polysulfide conversion and Li_2S decomposition [51].

Experimentally, Zhang et al. incorporated trace amounts of MoB MBene into carbon nanofiber/sulfur cathodes and achieved an initial discharge capacity of 1105 mAh g^{-1} at 0.2C and a capacity decay rate of only 0.0779 % per cycle over 800 cycles at 1C [51]. Li et al. used a MoAlB-derived MBene/carbon nanotube composite as a sulfur host and attained 768.0 mAh g^{-1} after 100 cycles at 1C with a practical sulfur loading of 3.8 mg cm^{-2} [248]. These results highlight the dual adsorptive-catalytic role of MBenes in Li-S chemistry and illustrate how trace amounts of MBenes can effectively trigger catalytic conversion of polysulfides.

6.6.3 Supercapacitors and Novel Battery Systems

Supercapacitor results likewise belong to different product and measurement configurations. The partially Al-depleted multilayer $\text{MoAl}_{1-x}\text{B}$ film in Ref. [16] gave a single-electrode-normalized areal capacitance of $2006.6 \text{ mF cm}^{-2}$ ($1003.3 \text{ mF cm}^{-2}$ for the symmetric device), derived from CV at 1 mV s^{-1} in 1 M Na_2SO_4 and retained 80.2% after 5000 cycles at 6 mA cm^{-2} . A later study of single/few-layer MoB reported $4025.6 \text{ mF cm}^{-2}$ from galvanostatic discharge at 5 mA cm^{-2} in a three-electrode configuration with 1 M Na_2SO_4 [205], providing a distinct product state from the partially Al-depleted material in Ref. [16]. Aghamohammadi et al. reported 20.3 mF cm^{-2} and 92% retention after 1300 cycles for an all-solid-state flexible interdigitated device [54]. The reported capacitances use different scan/current conditions, cell configurations and normalization bases. Rare-earth-containing *i*-MAB precursors and their etched derivatives were also investigated for magnetic and supercapacitor behavior [25]; the resulting composition depends on the extent of rare-earth removal.

Br-bearing MBenes extend storage beyond simple ion intercalation. An I₂-hosting MBene-Br cathode operated through coupled iodine and bromine redox processes over 0.4–2.1 V [47]. Tests used CR-2032 cells with a Zn negative electrode and 21 m LiTFSI + 1 m Zn(OTf)₂ aqueous electrolyte; the carbon-cloth positive electrode contained active material, Ketjen Black and PVDF in a 7:2:1 mass ratio. The composite contained 21.1 wt% iodine. The reported discharge capacity of 401.3 mAh g⁻¹ at 1 A g⁻¹ was normalized to the mass of I₂ in I₂@MBene-Br, although both iodine and Br terminations contributed to charge storage. The separate capacity of 143.8 mAh g⁻¹ for MBene-Br was normalized to the mass of MBene-Br. The average electrode loading was 4.5–5.5 mg cm⁻². The study also reported 485.8 Wh kg⁻¹ at 899.7 W kg⁻¹ and a maximum power density of 6007.7 W kg⁻¹ at 180.2 Wh kg⁻¹ (mass basis not specified). Nitrogen-doped boridene was also investigated as a cathode catalyst in Mg–CO₂ batteries, with a reported energy efficiency of 93.6% and operation over 305 cycles at 200 mA g⁻¹ [249].

6.6.4 Electrocatalysis and Photocatalysis

(1) Electrocatalysis

MBenes have attracted intense interest as electrocatalysts, particularly for the hydrogen evolution reaction (HER). Theoretical screening has identified numerous MBene compositions, including h-ZrBO, h-MoBO, and h-Nb₂BO₂, with near-zero hydrogen adsorption Gibbs free energy (ΔG_{H^*}), providing candidates for subsequent kinetic and experimental evaluation [35,38]. Experimentally, Park et al. demonstrated that delaminated MoAl_{1-x}B MBene sheets decorated with Pt single atoms (Pt–

MoAl_{1-x}B) exhibit ultralow overpotentials of 32 mV in alkaline and 18 mV in acidic media at 10 mA cm⁻², with Pt/C comparisons reported under the study's protocols [27]. Wang et al. successfully synthesized the computationally predicted bimetallic *i*-MBene Mo₂ErB₃T_{2.5} and measured an HER overpotential of 70 mV at 10 mA cm⁻² in 0.5 M H₂SO₄, demonstrating an experimentally tested parent–derivative pair within the computational screening workflow [28].

Beyond HER, MBenes are being explored for the nitrogen reduction reaction (NRR) and the CO₂ reduction reaction (CO₂RR). First-principles studies identify Mo₂B₂ and Cr₂B₂ [58], and Mo₃B₄ and Cr₃B₄ [59], as candidate CO₂RR catalysts with low limiting potentials and selectivity over the competing HER. For NRR, metal-vacancy-enriched boridene nanosheets (Mo_{4/3}B_{2-x}T_z) achieved a Faradaic efficiency of 66.7% at -0.2 V vs RHE and a maximum NH₃ yield rate of 23.6 µg h⁻¹ mgcat⁻¹ at -0.4 V vs RHE [250]. FeS₂-MBene heterostructures separately delivered a reported NH₃ yield rate of 37.13 ± 1.31 µg h⁻¹ mgcat⁻¹ with a Faradaic efficiency of 55.97 ± 2.63% at -0.2 V vs RHE [251], highlighting the synergy between MBene substrates and transition-metal/sulfide active centers.

(2) Photocatalysis

MBenes have also emerged as efficient noble-metal-free co-catalysts for photocatalytic hydrogen evolution. Jin et al. integrated MoB MBene with CdS semiconductors and obtained a remarkable H₂ production rate of 16 892 µmol g⁻¹ h⁻¹ under visible light, exceeding that of pure CdS under the same conditions [252]. The enhancement was attributed to improved visible-light absorption (red-shifted

absorption edge), promoted charge separation as evidenced by photoluminescence quenching, and extended carrier lifetimes. Other MBene-based photocatalytic systems, such as CrB/Cd_{0.8}Zn_{0.2}S Schottky heterojunctions [253] and black-phosphorus/MXene/MBene ternary heterostructures [254], have also demonstrated synergistic charge-transfer benefits, supporting further tests of specific heterostructures under matched light spectra, catalyst loadings and reaction conditions.

6.6.5 Gas Sensing and Optoelectronic Devices

MBenes have demonstrated notable advantages in gas sensing, particularly for nitrogen dioxide (NO₂). Zhang et al. fabricated SnS₂/Mo_{4/3}B₂ MBene microcomposites for room-temperature NO₂ detection, achieving a response of 4.82 toward 1 ppm NO₂ and an ultralow detection limit of 0.1 ppb. The NO₂ response exceeded that of SnS₂/Ti₃C₂ composites with similar microstructure and component ratio, and the sensor also showed good selectivity and repeatability [55]. Complementary DFT calculations confirmed that the MBene component provides stronger adsorption sites for NO₂ molecules, underpinning the enhanced sensing mechanism. Separately, Liu et al. exploited the hydrophilic surface of fluorine-free MoBT_x MBene to construct a humidity sensor with a 90% response at 98% relative humidity and a resolution of 1% relative humidity at room temperature [56]. The investigated product was multilayer MoBT_x with O, OH and Cl surface species. Water adsorption and intercalation contribute to the measured resistance response.

In an experimental optoelectronic device, an MBene-containing interlayer was

inserted at the buried SnO₂/perovskite interface in perovskite solar cells (PSCs). A combination of X-ray photoelectron spectroscopy, ultraviolet photoelectron spectroscopy, and DFT analyses revealed that MBene transfers electrons to the SnO₂ electron-transport layer, forming Mo–O–Sn covalent bonds and an interfacial dipole that optimizes energy-level alignment, enhances charge extraction, and passivates interfacial defects. The resulting PSCs achieved a power conversion efficiency of 24.32 % with substantially improved operational stability [255]. Furthermore, Mo_{4/3}B_{2-x}T_z/Si van der Waals Schottky photodiodes have demonstrated ultrahigh detectivity for color single-pixel imaging [256], while Mo_{4/3}B₂T₂/TiO₂ van der Waals heterostructures have been demonstrated as saturable absorbers for ultrafast pulse generation [257], underscoring the versatility of MBenes in photonic and optoelectronic applications.

6.6.6 Emerging Applications and Comparative Outlook

Beyond the main application categories discussed above, MBenes are rapidly expanding into a variety of other frontier areas. In electromagnetic wave attenuation and shielding, hierarchical MBene/MoS₂ heterostructures with controllable mesoporous wrinkling have shown effective microwave attenuation [258], while ab initio calculations have evaluated the shielding efficiency of two-dimensional FeB and Fe₂B iron boride nanostructures, which were classified as members of the MBene family in that work [259]. MBene membranes and aerogels have been employed for solar-driven interfacial evaporation, using the reported membrane or aerogel configurations for solar-driven freshwater production [260,261]. The photothermal

effect of boride nanosheets has also been investigated for therapeutic purposes: Chen et al. developed hyaluronic-acid-functionalized zirconium boride nanosheets (ZBN–HA) for photocontrolled intratumoral retention and drug release [218]. The illustration in Fig. 11(d) depicts tumor retention in a preclinical setting, whose biological response depends on the formulated material, dose and test model.

An additional experimental example is the ferromagnetic response reported for MnB-containing nanosheet powder produced by ZnCl_2 etching of Mn_2AlB_2 at a parent:salt molar ratio of 1:2 and 650°C for 4 h [29]. Vibrating-sample magnetometry gave a reported saturation magnetization of 42 emu g^{-1} and coercivity of 228 Oe at room temperature. Hysteresis loops measured at 100, 200, 300 and 400 K over -10 to $+10$ kOe retained a ferromagnetic response at 400 K; this is the highest measured temperature in that series, not a measured Curie temperature. ICP-OES reported 25.87 wt% residual Zn in the etched product, and spectroscopy identified oxygen-containing species. The measured magnetic response thus pertains to the Zn- and oxygen-containing powder, whose composition differs from the ideal FeB, Fe_2B or MnB monolayers considered in calculations [29].

In the biomedical and environmental sensing domains, Yang et al. exploited the strong DNA adsorbability of MBene nanosheets to construct fluorescence biosensors and paper-based microfluidic devices for circulating tumor DNA (ctDNA) detection, demonstrating a proof-of-concept assay format [219]. The same group also demonstrated an electrochemical MBene-based paper sensor for ctDNA [262]. Jakubczak et al. investigated the interactions of MoAlB@MBene with bacterial cells

and revealed concentration-dependent antibacterial responses, ROS/singlet-oxygen generation, and unique material–cell interplays [263]. In agriculture, Jakubczak et al. recently compared the effects of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene and MoAlB@MBene on higher plants, revealing distinct concentration-dependent biological responses and highlighting the need for careful environmental assessment as MBene applications expand [220]. MBenes have also been applied as nanozymes for portable wireless intelligent sensing of food-related markers such as sesamol in sesame seeds [264], as adsorbents for pharmaceutical pollutants [265], and as model nanosheets for nanometabolomics-enabled biological assessment [266]. The discovery of room-temperature ferromagnetism in vacancy-engineered $\text{Mo}_{4/3}\text{B}_{2-x}$ MBene nanosheets [267] further opens possibilities for spintronic applications.

The strongest connection across this section is the dependence of function on the identified parent, transformation route and recovered product. Experiments on partial etching, terminated sheets, supported catalysts and composite devices address different material states from calculations on ideal monolayers. Together they define testable opportunities for storage, catalysis and sensing, while comparisons with MXenes require matched structures, surface chemistry and operating conditions. Scale, reproducibility and long-term performance remain topics for assessment rather than established family-wide attributes.

Across Section 6, the clearest structure–property links are those tied to a specified composition and measured material state: anisotropic deformation and fracture in selected bulk ceramics, Al-derived surface protection or tribofilms,

defect-specific irradiation response, and surface-dependent functions of identified derivatives. Tables 2, 6 and 7 summarize these complementary results. These distinctions motivate the composition, processing and characterization priorities in Section 7.

7. Conclusions and Outlook

7.1 Conclusions

Recent research has broadened the range of layered borides discussed as MAB phases and has developed synthesis routes and property–application relationships for representative compositions. Their classification continues to evolve; the conclusions below therefore follow the operational scope and subfamily distinctions stated in Sections 1 and 3.1. This review has traced their evolution from early Mo–Al–B reports in 1942 and early structural characterizations in the 1960s, through the discovery of the room-temperature magnetocaloric effect in Fe_2AlB_2 in 2013, the proposal of the unified MAB phase concept in 2015, the report of an Al-depleted layered CrB product in 2018, and the ongoing emergence of structurally novel variants including *i*-MAB, *h*-MAB, and *o*-MAB phases. Several major conclusions emerge from this systematic account.

(1) The MAB scope adopted in this review covers a diverse set of experimentally reported and theoretically predicted layered transition-metal borides and related subfamilies. The structures discussed span orthorhombic, tetragonal, hexagonal, and trigonal symmetries and involve multiple stoichiometric types, boron-network topologies, A-layer stacking arrangements, and in-plane or out-of-plane

chemical-ordering patterns. These descriptors are complementary rather than mutually exclusive, and the resulting structural diversity provides a broad design space for composition and property engineering.

(2) First-principles studies of representative conventional MAB phases, particularly the Cr–Al–B and Mo–Al–B systems, reveal a pronounced bonding hierarchy in which B–B and selected M–B interactions form a relatively stiff framework, whereas A-related interactions are generally more compliant. This picture provides a useful basis for interpreting anisotropic deformation, damage tolerance, and selective A-layer removal in the corresponding compositions. The related 211-type, non-Al and reconstructed derivatives require composition-specific bonding analysis.

(3) This review organizes computational stability evidence around competing-phase energetics, phonons and elastic response, with finite-temperature contributions where available. These assessments have guided the exploration of *i*-MAB and *o*-MAB phases [19,20,82], but the accepted candidate sets depend on each study's reference phases, models and screening thresholds. Their relation to practical synthesis is discussed in Section 4.1.5.

(4) Reported synthesis routes provide different product forms: HP and SPS produce consolidated bulk specimens, reaction and salt/combustion routes provide powders or reaction bodies, Al flux growth supplies individual crystals, and sputtering or aluminizing produces substrate-supported layers. Table 5 distinguishes phase content, relative density and isolated recovery for these product forms. Precursor

chemistry, thermal history, pressure and post-treatment jointly determine the usable product; Section 5.8 connects these variables to structural, functional and MBene-parent requirements.

(5) Selected experimentally synthesized MAB phases combine substantial hardness or strength with non-catastrophic fracture behavior, while reported transport, oxidation, tribological, magnetic, and radiation-related properties vary considerably among compositions and sample states. Representative Al-containing phases can form protective oxide scales, show oxidation-induced crack healing, or provide useful magnetocaloric and high-temperature responses. The semi-quantitative D_t comparisons and observed fracture mechanisms support further evaluation of these materials under matched test conditions.

(6) The experimental and theoretical derivation of two-dimensional MBenes from selected MAB precursors has broadened the functional scope of layered transition-metal borides. MBenes have been investigated in electrochemical energy storage, electrocatalysis, sensing, optoelectronics, photothermal conversion, and biomedical systems, while their performance depends strongly on parent-phase structure, etching or dealloying chemistry, vacancy content, surface terminations, and device configuration. The combined MAB–MBene platform therefore offers a useful connection between bulk structural ceramics and two-dimensional functional materials, but its technological maturity remains composition- and application-specific.

7.2 Outlook

While research activity in the field has expanded rapidly, the translation of MAB phases and MBenes into practical technologies remains at an early stage, constrained by several scientific and technological challenges discussed below.

7.2.1 Current Challenges

Challenge 1: Connecting predicted candidates with reproducible synthesis. For predicted MAB-phase compositions, experiments should identify suitable precursors and processing windows and quantify the resulting phase assemblages. Reporting unsuccessful routes alongside successful preparations would help determine whether discrepancies arise from missing competing phases, temperature-dependent energetics or kinetic barriers (Sections 4.1 and 5).

Challenge 2: Insufficient control over phase purity, stoichiometry, and microstructure. Achieving phase-pure MAB-phase materials with precisely controlled stoichiometry and well-defined microstructure remains challenging, particularly for multi-element quaternary systems, compositions involving volatile A-site species, and phases near thermodynamic boundaries. Impurity phases including binary borides, intermetallics, and oxide inclusions frequently coexist with the target phase, confounding property measurements and obscuring structure–property relationships. The independent and simultaneous control of grain size, crystallographic texture, defect density, and solid solution homogeneity, all of which critically influence both structural and functional performance, has not yet been systematically achieved for most MAB-phase compositions.

Challenge 3: Scalability and sustainability of fabrication processes. Most current synthesis routes operate at the laboratory scale and are hindered by one or more of the following limitations: high energy consumption from elevated-temperature sintering, reliance on expensive or high-purity elemental precursors, necessity for protective inert atmospheres, low throughput of methods such as the aluminum flux technique, or lack of geometric versatility in die-based pressing methods. Scaling these processes to industrially relevant quantities while preserving phase purity, microstructural uniformity, and compositional accuracy remains a significant challenge.

Challenge 4: Incomplete mechanistic understanding at the atomic scale. Despite the productive application of first-principles calculations to ground-state properties, the atomic-scale mechanisms governing many key dynamic behaviors of MAB phases, including deformation and plasticity, high-temperature creep and diffusion, oxidation kinetics and scale growth, radiation damage accumulation and annealing, and electrocatalytic reaction pathways, are not fully understood. This knowledge gap arises partly from the scarcity of real-time, in-situ characterization data collected under realistic operating conditions, and partly from the difficulty of bridging the temporal and spatial scales between atomistic simulations and macroscopic experimental observations.

Challenge 5: Performance under multi-field coupled extreme conditions. While individual properties such as oxidation resistance, radiation tolerance, and tribological behavior have been investigated in isolation under well-defined laboratory conditions, the long-term service performance of MAB phases under simultaneously applied

extreme stimuli, representative of real engineering environments such as nuclear reactors, hypersonic propulsion systems, and high-temperature turbines, has been barely explored. The interaction among thermal, mechanical, chemical, and irradiation fields during service can give rise to synergistic degradation mechanisms that are qualitatively and quantitatively distinct from any individual degradation mode.

Challenge 6: Product identity and reproducibility of MBenes. The relationship between residual A content, layer number, reconstruction and surface chemistry remains incompletely mapped for many compositions. Studies should report these quantities together with phase impurities and recovery, so that an isolated monolayer, a multilayer etched particle and a partially depleted parent can be distinguished. Long-term chemical stability also requires a defined environment and direct degradation measurements; device-response retention alone does not resolve it.

Challenge 7: Underdeveloped structure–property relationships and materials databases. Compared to the extensively characterized MXene family, the fundamental structure–property relationships of MBenes, including the effects of structural polymorph, surface termination type, interlayer spacing, vacancy concentration, and defect configuration on electrochemical, catalytic, magnetic, mechanical, and optical properties, are only beginning to be elucidated. Comprehensive, standardized, and openly accessible experimental databases for both MAB phases and MBenes are largely absent, hampering data-driven research and the development of predictive property models applicable across the compositional space.

7.2.2 Future Directions

Guided by the challenges identified above, the following research directions are expected to drive the future development of the MAB phase field.

Direction 1: Data-guided discovery with explicit validation. Future workflows should report training coverage, prediction uncertainty and the competing phases included in each search, then validate selected candidates with independent DFT calculations and targeted synthesis. Linking these results to measured phase purity and processing conditions would make the methods discussed in Section 4.1.5 more useful for selecting the next experiments.

Direction 2: Development of green, scalable, and precision synthesis technologies. For bulk structural applications, the further optimization of spark plasma sintering, molten salt synthesis, and self-propagating high-temperature synthesis, combined with advances in precursor design, reaction pathway engineering, and process control, is needed to achieve efficient, reproducible fabrication of high-purity, high-performance MAB-phase materials with complex compositions at commercially viable scales. For MBene production, fluorine-free methods should be assessed through selectivity, recovered yield, reagent consumption and waste treatment, rather than assumed to be environmentally benign. Product-form criteria are discussed in Section 5.9; application-specific surface optimization is addressed in Direction 6.

Direction 3: Multi-scale mechanistic understanding through in-situ characterization and coupled simulation. The deployment of advanced in-situ and operando characterization techniques, including synchrotron X-ray diffraction,

aberration-corrected electron microscopy, atom probe tomography, and neutron scattering, under realistic operating conditions will enable direct visualization of the structural evolution, defect dynamics, and phase transformation processes that underlie key functional behaviors. These experimental observations must be systematically integrated with multi-scale computational frameworks that bridge density functional theory, molecular dynamics, and continuum mechanics models, with the ultimate goal of constructing quantitatively predictive structure–property relationships applicable across temperature, composition, and loading condition.

Direction 4: Systematic evaluation and design for coupled extreme environments.

A dedicated and systematic research program should be established to evaluate the long-term performance and failure mechanisms of MAB phases under multi-field coupled extreme conditions representative of their intended service environments, including combined high-temperature oxidation and mechanical loading, simultaneous irradiation and thermal cycling, tribocorrosion, and ablation under hypersonic flow. Establishing internationally standardized testing protocols, building comprehensive performance databases, and developing physics-based lifetime prediction models will be indispensable for enabling materials qualification for critical structural applications.

Direction 5: Compositional engineering for targeted property optimization.

Solid solution formation at M, A, and B sites, as well as the design of in-plane and out-of-plane chemically ordered quaternary and quinary MAB phases, offer powerful and largely unexploited levers for independently tuning hardness, toughness,

oxidation resistance, thermal conductivity, radiation tolerance, and functional performance. First-principles-guided alloying design, integrated with high-throughput experimental synthesis and multi-property characterization, should be employed to systematically map performance landscapes across compositional space and to identify compositions that simultaneously satisfy multiple, sometimes competing, engineering performance targets.

Direction 6: Testable surface and defect design of MBenes. Compare identified termination or defect states within the same composition and device protocol, then use operando measurements and calculations on those states to test the proposed adsorption or transport mechanism. Report changes in activity together with dissolution, reconstruction and performance retention. Such tests connect the product-identification problem in Challenge 6 with a measurable functional outcome.

Direction 7: Application-driven research toward practical deployment. As fundamental understanding and synthesis control mature, research priorities should increasingly shift toward application-targeted investigations in technologically impactful areas. These include high-entropy MAB-phase ceramics for thermal protection in hypersonic vehicles, radiation-tolerant cladding materials and neutron absorbers for advanced fission and fusion reactors, wear-resistant coatings for extreme tribological applications, next-generation electrode materials for solid-state batteries and green hydrogen production, and MBene-based flexible sensors, photodetectors, and biomedical diagnostic platforms. Progress toward these applications will depend on close coordination between synthesis, characterization,

and device engineering, and will ultimately determine the practical role of MAB phases and MBenes in energy, aerospace, nuclear, and information technologies.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (52472079), Sichuan Science and Technology Program (2025YFHZ0082, 2026NSFSC1227), and Fundamental Research Funds for the Central Universities (2682025CX095).

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