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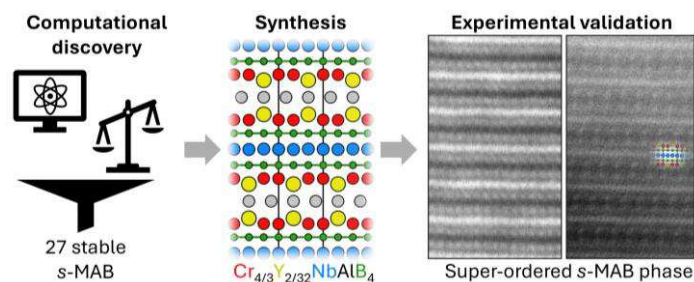
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Abstract

Chemical ordering provides a powerful route for expanding the structural diversity and tunability of layered borides. While in-plane chemical order has been established in hexagonal *i*-MAB phases, and out-of-plane order is well known in related layered carbide and boride systems, the simultaneous realization of both ordering modes within a single MAB phase structure is unexplored. Here, we computationally investigate super-ordered MAB phases, denoted *s*-MAB, as a family of layered borides combining in-plane and out-of-plane chemical ordering. The term “super-ordered” refers to the superposition of these two ordering motifs. Using first-principles calculations based on density functional theory, we systematically evaluate the thermodynamic stability of quinary 314 and 416 compositions, $M1_{4/3}M2_{2/3}M3AlB_4$ and $M1_{4/3}M2_{2/3}M3_2AlB_6$, where M1 and M3 are transition metals and $M2 = \text{Sc or Y}$. The screening identifies 26 *s*-MAB compositions predicted to be thermodynamically stable within the considered set of competing phases, of which 25 are also dynamically stable. The stable candidates most commonly contain $M1 = \text{Cr, Mo, W, Mn, or Fe}$, $M2 = \text{Y}$, and $M3 = \text{V, Nb, or Ta}$. Furthermore, electronic-structure calculations of *s*-MAB phases show metallic behavior, while the calculated Young’s, shear, and bulk moduli of selected 314 *s*-MAB compositions are approximately 20% larger than those of their corresponding 212 *i*-MAB reference phases. Guided by the predictions, we performed proof-of-concept synthesis targeting $\text{Cr}_{4/3}\text{Y}_{2/3}\text{NbAlB}_4$. The resulting multiphase material contains layered Cr-Y-Nb-Al-B grains whose local contrast in scanning transmission electron microscopy and elemental distribution from energy-dispersive X-ray spectroscopy are consistent with the predicted structural motif of separated Nb and Cr/Y-containing layers. Hence, the observations support the experimental feasibility of the predicted structural motif. These results provide a theory-guided map of candidate *s*-MAB phases for future synthesis and illustrates how coupled in-plane and out-of-plane ordering can expand the structural and compositional space of layered borides. Their potential two-dimensional derivatives may also allow for greater compositional flexibility than currently available two-dimensional borides (MBenes).



First-principles calculations predict a family of quinary s-MAB phases combining in-plane and out-of-plane metal ordering, while exploratory synthesis provides evidence consistent with the predicted structural motif.

1. Introduction

Binary transition metal borides have long been recognized for their outstanding properties, including high melting point, hardness, electrical and thermal conductivity, and resistance to corrosion,¹ making them valuable for applications like wear-resistant coatings and high-temperature components.²⁻⁵ Beyond function, transition metal borides exhibit a structural diversity stemming from varied bonding motifs and metal-to-boron ratios.⁶⁻⁷ This structural richness extends to layered ternary borides, also referred to as MAB phases.⁸⁻⁹

The first MAB phases discovered was Mn_2AlB_2 in 1966,¹⁰ followed by Cr_2AlB_2 and Fe_2AlB_2 .¹¹⁻¹³ These so-called 212 MAB phases are illustrated in Figure 1a and feature laminated structures with M-B sublattices interleaved by A-element layers. Many early MAB phases, including the extended series encompassing compositions like Cr_3AlB_4 and Cr_4AlB_6 (short notation 314 and 416, respectively, based on their M:A:B ratios), adopt orthorhombic crystal structures, often characterized by zigzag boron chains (see Figure 1a).^{9,11} Their general notation is $\text{M}_{n+1}\text{AB}_{2n}$. The family of MAB phases was expanded with the discovery of hexagonal Ti_2InB_2 ,¹⁴ the first MAB phase deviating from the common orthorhombic symmetry (Figure 1b). Later, a higher-order hexagonal V_3PbB_4 was reported.¹⁵ The hexagonal lattice, featuring flat honeycomb boron layers, is critical for enabling in-plane chemical ordering on the metal sites, leading to the discovery of *i*-MAB phases, such as $\text{Mo}_{4/3}\text{Sc}_{2/3}\text{AlB}_2$ and $\text{Mo}_{4/3}\text{Y}_{2/3}\text{AlB}_2$, as illustrated in Figure 1f.¹⁶⁻¹⁷ Such structure relates to the known *i*-MAX phases with in-plane chemical order of the two metals.¹⁸⁻¹⁹ Another type of chemical ordering is out-of-plane order in hexagonal *o*-MAX phases.²⁰⁻²¹ For MAB phases, out-of-plane ordering has been reported for related tetragonal M_5SiB_2 borides,²² as exemplified by *o*-MAB phases $\text{Ti}_4\text{MoSiB}_2$,²³ M_4CrSiB_2 (M = Mo, W, Nb),²⁴ and Ta_4MSiB_2 (M = V, Cr).²⁵ However, out-of-plane ordering analogous to that of *o*-MAX phases has not yet been established within the conventional orthorhombic or hexagonal MAB frameworks shown in Figure 1. This is in contrast with orthorhombic structures where alloying on the M- or A-site has so far only resulted in solid-solution, e.g., $(\text{Mn,Fe})_2\text{AlB}_2$,²⁶ $(\text{Cr,Mn})_3\text{AlB}_4$,²⁷ and $\text{Fe}_2(\text{Al,Ge})\text{B}_2$.²⁸ Synthesized MAB phases reported and restricted to orthorhombic and hexagonal symmetries are listed in Table 1.

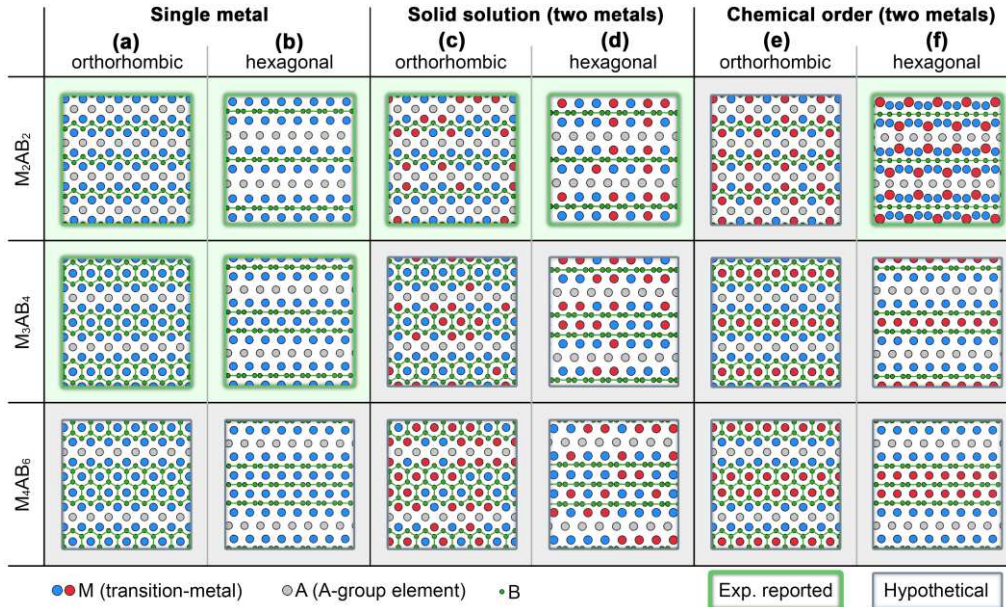


Figure 1. Schematic illustration of known and hypothetical layered MAB phases with (a,c,e) orthorhombic and (b,d,f) hexagonal symmetry. (a,b) Ternary MAB phases based on one metal in M_2AB_2 , M_3AB_4 , and M_4AB_6 composition. (c,d) Quaternary MAB phases with metal site solid solution. (e,f) Quaternary MAB phases with chemical order of metals in-plane for M_2AB_2 (*i*-MAB) or out-of-plane for M_3AB_4 and M_4AB_6 (*o*-MAB). Metal atoms represented by blue and red, A atoms in grey and boron atoms in green. Experimentally reported structures are framed by green squares whereas hypothetical, not yet reported structures, are framed by gray squares.

The demonstrated ability to engineer both *i*-MAX and *o*-MAX ordering within the hexagonal MAX lattice, and the recent discovery of combined in-plane and out-of-plane chemical ordering in super-ordered MAX phases (*s*-MAX),²⁹ serves as an inspiration for exploring similar structural and compositional complexity among MAB phases. Notably, all of the aforementioned MAX phase types have also been converted to 2D MXenes. The term “super-ordered” refers to the superposition of two distinct ordering motifs; (i) in-plane ordering within the outer metal layers and (ii) out-of-plane segregation between crystallographically distinct metal layers. Building on the discovery of hexagonal *i*-MAB phases, we herein propose and investigate super-ordered MAB phases (*s*-MAB). These hypothetical structures would feature simultaneous in-plane (*i*-MAB type) and out-of-plane (*o*-MAB type) chemical ordering within a single hexagonal lattice, as illustrated conceptually for 314 and 416 compositions in Figure 2. Like *i*-MAB phases,¹⁶ the stacking of one in-plane ordered M_{1/3}M_{2/3} layer to another M_{1/3}M_{2/3} layer can come in different variations, as illustrated by the three different crystals structures of space groups *P6/mmm*, *R-3m* and *P6₃/mmc*. Note that the in-plane order is only seen along specific axis, such as $[11\bar{2}0]$, whereas along $[11\bar{0}0]$ M1 and M2 overlap in projection. While out-of-plane ordering in borides have been reported for tetragonal T2-phases, such as Ti₄MoSiB₂²³ and Ta₄VSiB₂²⁵, to date, neither standalone hexagonal *o*-MAB phase nor the combined *s*-MAB structure have been experimentally synthesized, representing an open challenge for designing layered boride-based materials.

Table 1. Synthesized MAB phases for structures illustrated in Figure 1 and grouped according to crystal system, composition, and space group symmetry.

Crystal system	Short notation	MAB phase	Space group	Note	Reference
Orthorhombic	212	Cr ₂ AlB ₂	<i>Cmmm</i> (#65)		9, 11
		Mn ₂ AlB ₂	<i>Cmmm</i> (#65)		10
		Fe ₂ AlB ₂	<i>Cmmm</i> (#65)		12-13
		(Cr,Mn) ₂ AlB ₂	<i>Cmmm</i> (#65)	Disorder of Cr and Mn	27
		(Mn,Fe) ₂ AlB ₂	<i>Cmmm</i> (#65)	Disorder of Mn and Fe	26
		(Fe,Co) ₂ AlB ₂	<i>Cmmm</i> (#65)	Disorder of Fe and Co	30
		Fe ₂ (Al,Ga)B ₂	<i>Cmmm</i> (#65)	Disorder of Al and Ga	28
		Fe ₂ (Al,Ge)B ₂	<i>Cmmm</i> (#65)	Disorder of Al and Ge	28
		Fe ₂ (Al,Ga,Ge)B ₂	<i>Cmmm</i> (#65)	Disorder of Al, Ga, and Ge	28
	314	Cr ₃ AlB ₄	<i>Pmmm</i> (#47)		9, 11
		(Cr,Mn) ₃ AlB ₄	<i>Pmmm</i> (#47)	Disorder of Cr and Mn	27
	416	Cr ₄ AlB ₆	<i>Cmmm</i> (#65)		9
Hexagonal	212	Ti ₂ InB ₂	<i>P-6m2</i> (#187)		14
		Ti ₂ SnB ₂	<i>P-6m2</i> (#187)		31
		Hf ₂ InB ₂	<i>P-6m2</i> (#187)		15
		(Ti,Hf) ₂ InB ₂	<i>P-6m2</i> (#187)	Disorder of Ti and Hf	32
		Mo _{4/3} Sc _{2/3} AlB ₂ (<i>i</i> -MAB)	<i>R-3m</i> (#166)	In-plane order of Mo and Sc	16
		Mo _{4/3} Y _{2/3} AlB ₂ (<i>i</i> -MAB)	<i>R-3m</i> (#166)	In-plane order of Mo and Y	16
		Mo _{4/3} Tb _{2/3} AlB ₂ (<i>i</i> -MAB)	<i>R-3m</i> (#166)	In-plane order of Mo and Tb	33
		Mo _{4/3} Dy _{2/3} AlB ₂ (<i>i</i> -MAB)	<i>R-3m</i> (#166)	In-plane order of Mo and Dy	34
		Mo _{4/3} Ho _{2/3} AlB ₂ (<i>i</i> -MAB)	<i>R-3m</i> (#166)	In-plane order of Mo and Ho	33
		Mo _{4/3} Er _{2/3} AlB ₂ (<i>i</i> -MAB)	<i>R-3m</i> (#166)	In-plane order of Mo and Er	33
		Mo _{4/3} Tm _{2/3} AlB ₂ (<i>i</i> -MAB)	<i>R-3m</i> (#166)	In-plane order of Mo and Tm	34
		Mo _{4/3} Lu _{2/3} AlB ₂ (<i>i</i> -MAB)	<i>R-3m</i> (#166)	In-plane order of Mo and Lu	34
	314	V ₃ PB ₄	<i>P-6m2</i> (#187)		15

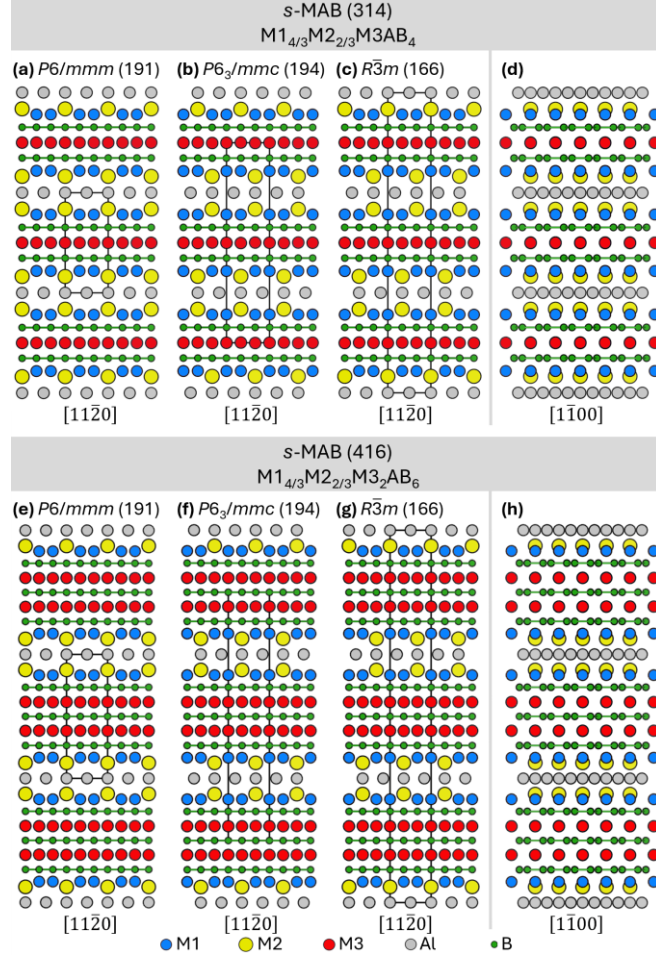


Figure 2. Schematic illustration of combined in- and out-of-plane chemical order in (a-d) 314 *s*-MAB and (e-g) 416 *s*-MAB phases with space group symmetry (a,e) $P6/mmm$ (#191), (b,f) $P6_3/mmc$ (#194) and (c,g) $R\bar{3}m$ (#166). (a-c,e-g) Structure seen along $[11\bar{2}0]$ and (d,h) $[1\bar{1}00]$ zone axis. Metal atoms represented by blue, yellow, and red, A atoms in grey and boron atoms in green. Unit cell represented by black box.

We hypothesize that the same structural limits and bonding preferences that favor hexagonal in-plane ordering in *i*-MAB phases may also help stabilize the additional but so far unreported out-of-plane ordering in hexagonal MAB phases. This represents a more restrictive design problem than conventional size-driven in-plane ordering. In addition to a sufficiently large M1 to M2 size mismatch, formation of an *s*-MAB phase requires M1 and M3 to preferentially occupy chemically distinct outer and inner metal layers and for the resulting ordered *s*-MAB structure to also remain energetically competitive with partially and fully disordered configurations. To address this, we use first-principles calculations based on density functional theory to systematically study the thermodynamic stability of possible quinary 314 and 416 *s*-MAB phases with M1_{4/3}M2_{2/3}M3AlB₄ and M1_{4/3}M2_{2/3}M3₂AlB₆ compositions, respectively. Here, M1 and M3 are different transition metals (Sc, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Fe) and M2 = Sc or Y. The selection of Sc and Y is motivated because their larger atomic size in the outer metal layer can promote in-plane ordering, as shown previously for *i*-MAB phases^{16, 35} and *i*-MAX phases.^{18, 36} By evaluating stability against a comprehensive set of competing phases, including disordered atomic configurations in MAB phases (Figure 1c,d), this study provides theoretical guidance for the targeted synthesis of new *s*-MAB compounds. Beyond expanding the accessible MAB phase chemistry, such ordering creates chemically inequivalent metal layers and directional bonding environments that may influence electronic structure, mechanical response, magnetic interactions, composition and characteristics of potential two-dimensional derivatives.

2. Method

2.1. Computational details

All calculations were performed within the framework of density functional theory (DFT) as implemented in Vienna Ab-initio Software Package (VASP) version 5.4.4,³⁷⁻³⁹ with the projector augmented wave (PAW) method and a planewave basis set expanded to a kinetic energy cutoff of 520 eV.⁴⁰⁻⁴² The Perdew–Burke–Ernzerhof (PBE) functional was used to describe the electron exchange-correlation effects,⁴² and all PBE potentials used are listed in Table S1. We used a Γ -centered k -point sampling, with a density of $0.1 \text{ \AA}^{-1}$.⁴³ All calculations were spin-polarized with an initial magnetic moment of three for the metal sites in a ferromagnetic (FM) spin configuration. Structures were fully relaxed in terms of volume, shape, and atomic positions using an energy convergence of $10^{-7} \text{ eV atom}^{-1}$ and a force convergence of $0.001 \text{ eV \AA}^{-1}$. Phonon dispersion spectra were calculated for s -MAB phases in $2 \times 2 \times 1$ primitive cells (96 and 132 atom supercells), by using the finite displacement method as implemented in Phonopy.⁴⁴

For thermodynamic phase stability predictions of a targeted phase (composition), the set of most competing phases, known as equilibrium simplex, is identified among all competing phases using a linear optimization procedure.⁴⁵⁻⁴⁶ This approach has been proven successful to confirm already experimentally synthesized materials as well as predicting the existence of new ones.^{19, 21, 36, 47-48} The stability of an s -MAB phase is quantified in terms of the formation enthalpy, $\Delta H_{\text{cp}}^{s\text{-MAB}}$, by comparing its energy, $E[s - \text{MAB}]$, to the energy of the equilibrium simplex, $E(\text{equilibrium simplex})$, at a given composition according to

$$\Delta H_{\text{cp}}^{s\text{-MAB}} = E[s - \text{MAB}] - E(\text{equilibrium simplex}). \quad (1)$$

A phase is considered stable if $\Delta H_{\text{cp}}^{s\text{-MAB}} < 0$, indicating a phase being energetically favored as compared to decomposition into its most competing phases, whereas $\Delta H_{\text{cp}}^{s\text{-MAB}} > 0$ indicates that decomposition is more energetically favorable. The complete set of competing phases considered herein encompasses those found in Materials Project database (v2021.05.13),⁴⁹ as well as ternary MAB phases,⁴⁷ quaternary MAB phases with in-plane order (i -MAB phases)¹⁶ and out-of-plane order (o -MAB phases),^{23, 50} and disordered solid solutions.²⁷ In addition, hypothetical phases based on structures illustrated in Figure 1, including quinary 314 and 416 s -MAB phases considered in this work, have also been accounted for as competing phases. All ordered s -MAB models contain the in-plane supercell required to represent the 2:1 distribution of M1 and M2 in the outer metal layers. Extension along the stacking direction was used to represent the three possible stackings of successive in-plane ordered layers, giving the $P6/mmm$, $P6_3/mmc$, and $R\bar{3}m$ structural variants shown in Figure 2. These models represent high-symmetry candidate stackings rather than an exhaustive enumeration of stacking faults, intergrowths, or lower-symmetry distortions.

Furthermore, to model configurational disorder on the M1 and M3 sites in s -MAB, so-called partial disorder since M2 is ordered in-plane in the outer metal layers, the special quasi-random structures (SQS) method as implemented in Alloy Theoretic Automated Toolkit (ATAT) was used to generate supercells with metals distributed in a disordered fashion.⁵¹⁻⁵² The SQS approach compares the correlation functions of a finite supercell to those of an infinite, ideal random system, providing structures that closely approximate near-random arrangements of metals. Herein we have used different supercell sizes for modelling partial disorder and full disorder composed of 168(165) and 144(198) atoms for 314(416) s -MAB and MAB phases, respectively.

When $T \neq 0 \text{ K}$, the contribution from configurational entropy for a disordered distribution of, e.g., M1 and M2, in a general compound α , where α represent both s -MAB phases and other competing phases, will decrease the Gibbs free energy as approximated by

$$G_{\alpha}(T) = H_{\alpha} - T\Delta S_{\alpha}, \quad (2)$$

where T is the temperature and ΔS_α is the entropic contribution. The configurational entropy, assuming an ideal solid solution of metals i on the M-sites, is estimated using a mean-field approach and is given by

$$\Delta S_\alpha = - \frac{k_B w \sum_m \sum_i^{N_m} a_m x_i^m \ln x_i^m}{\sum_m a_m}, \quad (3)$$

where k_B is the Boltzmann constant (in eV/K), w is the fraction of sites with respect to the entire supercell on which disorder is modelled upon, index m represents the sublattice, a_m is the number of sites of sublattice m , N_m is the total number of different metals in sublattice m , and x_i^m is concentration of metal i being randomly distributed on sublattice m . For a 314 s -MAB phase with partial disorder of M1 and M3 in a 4:3 ratio in a 168 atoms supercell, $w = 0.292$, $a_{M1} = 28$, $a_{M3} = 21$, $x_1^{M1} = 0.571$ (4/7), and $x_1^{M3} = 0.429$ (3/7). A 416 s -MAB phase with partial disorder of M1 and M3 in a 2:3 ratio in a 165 atoms supercell has $w = 0.303$, $a_{M1} = 20$, $a_{M3} = 30$, $x_1^{M1} = 0.4$, and $x_1^{M3} = 0.6$. At finite temperature, the stability of a s -MAB phase is therefore given by combining Eqs. 1, 2 and 3 into

$$\Delta G_{cp}^{s\text{-MAB}}(T) = E_{s\text{-MAB}} - G_{\text{equilibrium simplex}}(T). \quad (4)$$

To assess the influence of configurational entropy on the relative stability of ordered and disordered structures, the configurational contribution was evaluated at 2000 K for partially and fully disordered MAB phases as well as for disordered competing phases using. This temperature is near the upper end of the range commonly used for MAB phase synthesis and was deliberately selected to emphasize the stabilizing contribution, $-T\Delta S$, associated with sublattice disorder. Compared with the experimental synthesis temperature of 1648 K, use of 2000 K therefore favours configurations containing chemical disorder and provides a stringent test of whether fully ordered s -MAB structures remain competitive against entropy-driven disorder. Because both the target structures and their competing phases may contain disordered sublattices, the results should be interpreted as a common high-temperature screening condition rather than as a strict upper or lower bound on ΔG_{cp} . Vibrational, electronic, and magnetic free-energy contributions were not included.

Electronic band structures and densities of states were plotted using the *sumo* Python package.⁵³ The elastic properties were determined using VASPKIT and the stress-strain method.⁵⁴ The bulk modulus (B), shear modulus (G), and Young's modulus (E) were calculated based on the Voigt-Reuss-Hill approximation, with the reported values representing the Hill averages. Visualization of structures was performed using VESTA.⁵⁵

2.2. Material synthesis

The powders used for materials synthesis were Cr (Sigma Aldrich, 99%, -325 mesh), CrB₂ (Alfa Aesar, 99%, -325 mesh), NbB₂ (Alfa Aesar, 99%), Al (Thermoscientific, 99.5%, -325 mesh), and Y (Stanford Advanced Materials, 99.9%REM, -325 mesh). To obtain 1 gram of Cr_{4/3}Y_{2/3}NbAlB₄ (314 s -MAB), 0.252 g of CrB₂, 0.059 g of Cr, 0.393 g of NbB₂, 0.092 g of Al, and 0.203 g of Y were used. Powders were mixed thoroughly using an alumina mortar and pestle. The powder mixture was then placed into a die (Precision elements, 10 mm in diameter) and cold-pressed using a manual pellet press (Hench YP-15F, 13 MPa). The resultant pellet was inserted into an alumina crucible and sintered in a vacuum furnace (Siomm, SQHL-1000) at a base pressure of $3 \cdot 10^{-3}$ Pa. Temperatures used for sintering were 1350, 1375, 1400, 1450, 1500, and 1550 °C. Ramping rates were 7 °C/min and reaction times were 30, 60, and 90 minutes. The sample used for detailed characterization herein was sintered at 1375 °C for 30 minutes and then cooled at a rate of 10 °C/min to room temperature. After synthesis the oxidized surface of the pellet was removed by sandpaper then the pellet was crushed into loose powder, and sieved (VWR, 25 micron aperture).

2.3. Structural and compositional analysis

X-ray diffraction (XRD) scans of the Cr_{4/3}Y_{2/3}NbAlB₄ powder were carried out on PreFIX Panalytical diffractometer with a Bragg-Brentano setup (Cu K_α radiation source, 0.04 rad soller slits, 1/2° anti-scatter, 1/2° divergence slits, 5.5 mm receiving slit, Ni K_β filter, step-size 0.00835°, time-per-step of 20 s). Morphology and chemical composition analysis was carried out using a Zeiss sigma 300

scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDX), applied to selected individual $\text{Cr}_{4/3}\text{Y}_{2/3}\text{NbAlB}_4$ grains.

High-resolution scanning transmission electron microscopy (HRSTEM) was performed in the double-corrected Linköping FEI Titan3 using high angle annular dark field imaging (STEM-HAADF), equipped with an EDX detector and operated at 300 kV.

3. Results and Discussion

3.1. Phase stability screening for super-ordered MAB phases (s-MAB)

The search for MAB phases that combine in-plane chemical order, as in *i*-MAB phases,^{16, 33-34} with out-of-plane chemical order into super-ordered structures, here denoted *s*-MAB phases, requires a careful choice of metals. Similar to *i*-MAB phases, the minority metal in the outer metal layer, denoted M2 in Figure 2, should be significantly larger than the majority metal, denoted M1 in Figure 2. This condition is fulfilled when M2 = Sc or Y. Since it is not possible to know beforehand how the three metals M1, M2, and M3 will distribute within the MAB structure, we considered three different distributions: (i) the fully ordered *s*-MAB structure with three types of stackings (Figure 2), (ii) a partially disordered *s*-MAB structure, where M2 is ordered in-plane in the outer metal layer while M1 and M3 form a solid solution across the outer and inner metal layers (Figure S1b,e), and (iii) a fully disordered MAB structure, where M1, M2, and M3 form a solid solution across both outer and inner metal layers (Figure S1c,f). These models have the same composition but differ in how M1, M2, and M3 are distributed. Comparison of these models therefore tests not only whether a given composition can form a MAB-type structure, but also whether simultaneous in-plane and out-of-plane ordering is preferred over competing degrees of chemical disorder and competing phases.

The thermodynamic stability of 314 and 416 *s*-MAB phases, structures illustrated in Figure 2, was systematically studied encompassing compositions M1 and M3 = {Sc, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Fe}, M2 = {Sc, Y}, and A = Al. The choice of Sc and Y as M2 is based on their larger atomic size compared to other transition metals, which can promote in-plane ordering, an important condition for the formation of *i*-MAB phases.^{16, 35} Since MAB phases are usually synthesized at high temperatures, typically between 1000 and 1800 °C, corresponding to 1273 - 2073 K, the effect of configurational entropy on the Gibbs free energy should be included for structures with disordered metal distributions. The finite-temperature stability screening was therefore performed at 2000 K, with contribution to the ideal configurational entropy in partially (Figure S1b) and fully disordered MAB phases (Figure S1c) and disordered competing phases included through Eq. 2 and 3. The deliberately high temperature thus provides an overestimated stability for all disordered configurations. These competing phases include, for example, $(\text{M}_{1.0.67}\text{M}_{3.0.33})_2\text{AlB}_2$ with space groups *Cmmm* (Figure 1c) and *P-6m2* (Figure 1d), $(\text{M}_{1.0.5}\text{M}_{3.0.5})\text{AlB}$ with space group *Cmcm*, and metal borides such as $(\text{M}_{1-x}\text{M}_x)\text{B}_2$ and $(\text{M}_{1-x}\text{M}_x)\text{B}$. This approach gives a more realistic prediction of whether ordered or disordered metal distributions are likely to form during synthesis. Similar methods have previously been used successfully to guide experiments that led to the discovery of chemical order and disorder in several MAB phases.^{16, 23, 27, 35, 50}

The stability results for the 314 MAB phases are summarized in the heatmap in Figure 3 where the left and upper triangles show the stability of the fully ordered *s*-MAB phase in space groups *P6/mmm* (Figure 2a) and *R-3m* (Figure 2c). The right triangles show the partially disordered *s*-MAB phases, while the bottom triangles show MAB phases with complete disorder of M1, M2, and M3. In the heatmap, blue indicates stable phases, with $\Delta G_{\text{cp}}^{s\text{-MAB}}$ or $\Delta G_{\text{cp}}^{\text{disorder}} < 0$, while red indicates unstable or metastable phases, with $\Delta G_{\text{cp}}^{s\text{-MAB}}$ or $\Delta G_{\text{cp}}^{\text{disorder}} > 0$. More detailed information on stability and the most competing phases is given in Table S2 for M2 = Sc and Table S3 for M2 = Y. Black triangles in the heatmap mark compositions or elemental distributions that were not considered. This choice is based on the observation that when $\Delta G_{\text{cp}}^{s\text{-MAB}}$ is clearly above zero, meaning that the *s*-MAB phase is far from stable, the corresponding partially disordered or fully disordered structure is also unlikely to become stable, even after including configurational entropy. It should also be noted that the energies of the different *s*-MAB structures are often close to degenerate.

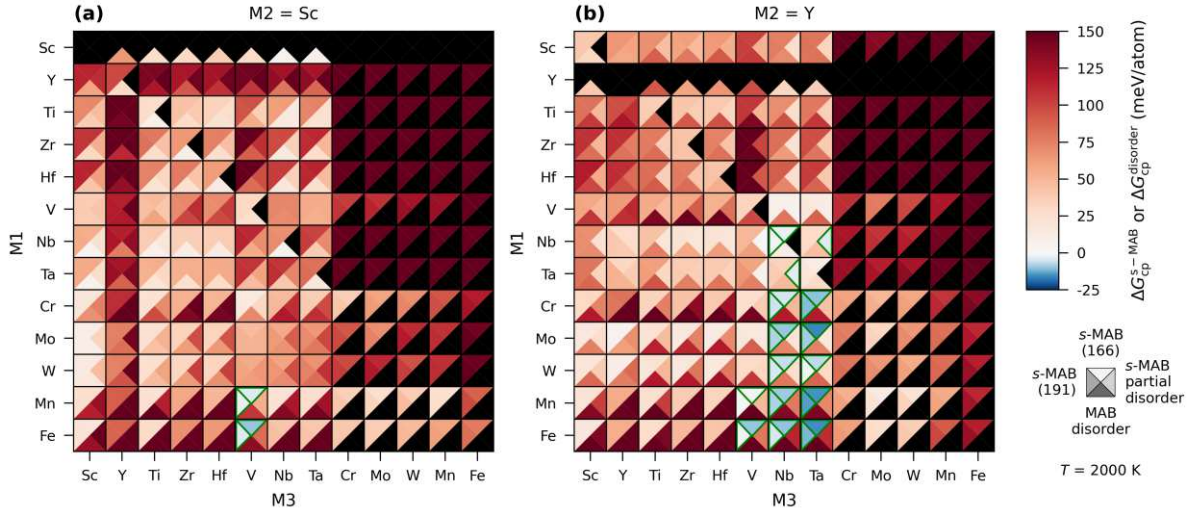


Figure 3. Stability heatmap for hexagonal 314 MAB phases, with configurational entropy included at 2000 K for partially and fully disordered structures and disordered competing phases, upon mixing metals M1, M2, M3 in a 4:2:3 ratio with (a) M2 = Sc and (b) M2 = Y. For a given combination of M1 and M3, the left and upper triangles indicate the stability for combined in- and out-of-plane ordered *s*-MAB in space group *P6/mmm* and *R-3m*, the right triangles indicate the stability for *s*-MAB with partial disorder, having in-plane order of M2 in the outer metal layer combined with disorder of M1 + M3, and the bottom triangles indicate the stability for MAB with disorder of M1, M2, and M3. Stable phases are framed in green. Filled black triangles represent combinations of M1, M2 and M3 not considered.

Among the investigated phases, 14 *s*-MAB phases of a 314 composition were found to be stable. For clarity, these are framed in green. Of these, 2 have M2 = Sc and 12 have M2 = Y. Examples include $\text{Cr}_{4/3}\text{Y}_{2/3}\text{NbAlB}_4$ with $\Delta G_{\text{cp}}^{s\text{-MAB}} = -5$ meV/atom and $\text{Mo}_{4/3}\text{Y}_{2/3}\text{TaAlB}_4$ with $\Delta G_{\text{cp}}^{s\text{-MAB}} = -16$ meV/atom. Detailed structural data (space group, lattice parameter, and Wyckoff position) for $\text{Cr}_{4/3}\text{Y}_{2/3}\text{NbAlB}_4$ are given in Table 2 for the three stackings illustrated in Figure 2. A common feature of the predicted stable *s*-MAB phases is that M1 is usually from Group 6 (Cr, Mo, W), Group 7 (Mn), or Group 8 (Fe), while M3 is from Group 5 metals (V, Nb, or Ta). Stable partially disordered *s*-MAB or fully disordered MAB phases are much less common. Only two such phases were identified, both involving Nb and Ta as M1 and M3. In addition, the dynamical stability of the stable *s*-MAB phases in Figure 3 was evaluated from their phonon dispersion spectra, shown in Figures S3-S16. All but one of these *s*-MAB phase are dynamically stable. The only exception is $\text{Fe}_{4/3}\text{Sc}_{2/3}\text{VAlB}_4$, which exhibits dynamical instability (Figure S4). One possible origin of this instability is that only a ferromagnetic spin configuration was considered. Including additional antiferromagnetic spin configurations may stabilize the structure, as has previously been demonstrated for related materials, such as *s*-MAX phases.⁵⁶

Table 2. Calculated structural data for $\text{Cr}_{4/3}\text{Y}_{2/3}\text{NbAlB}_4$ *s*-MAB in structures with *P6/mmm*, *P6₃/mmc*, and *R-3m* space group symmetry. Structural relaxation performed using GGA-PBE exchange-correlation functional. Note that data for *R-3m* is given in its hexagonal representation.

<i>s</i> -MAB	Space group	Lattice parameters	Wyckoff site
$\text{Cr}_{4/3}\text{Y}_{2/3}\text{NbAlB}_4$	<i>P6/mmm</i> no. 191	$a = b = 5.35222 \text{ \AA}$	Cr1: $4h$ (0.33333, 0.66667, 0.22144)
		$c = 10.6180 \text{ \AA}$	Y1: $2e$ (0.00000, 0.00000, 0.15985)
		$\alpha = \beta = 90^\circ$	Nb1: $2d$ (0.33333, 0.66667, 0.50000)
		$\gamma = 120^\circ$	Nb2: $1b$ (0.00000, 0.00000, 0.50000)
			Al1: $3f$ (0.50000, 0.00000, 0.00000)
			B1: $12n$ (0.66489, 0.00000, 0.33920)
$\text{Cr}_{4/3}\text{Y}_{2/3}\text{NbAlB}_4$	<i>P6₃/mmc</i> no. 194	$a = b = 5.34978 \text{ \AA}$	Cr1: $4e$ (0.00000, 0.00000, 0.86062)
		$c = 21.2363 \text{ \AA}$	Cr2: $4f$ (0.33333, 0.66667, 0.86095)
		$\alpha = \beta = 90^\circ$	Y1: $4f$ (0.33333, 0.66667, 0.33032)
		$\gamma = 120^\circ$	Nb1: $2a$ (0.00000, 0.00000, 0.00000)
			Nb2: $4f$ (0.33333, 0.66667, 0.49837)
			Al1: $6h$ (0.83346, 0.66692, 0.25000)

Cr _{4/3} Y _{2/3} NbAlB ₄	<i>R</i> -3 <i>m</i> (hexagonal axes) no. 166	<i>a</i> = <i>b</i> = 5.35088 Å <i>c</i> = 31.8486 Å <i>α</i> = <i>β</i> = 90° <i>γ</i> = 120°	B1: 24 <i>l</i> (0.66693, -0.00143, -0.08048)
			Cr1: 6 <i>c</i> (0.00000, 0.00000, 0.59301)
			Cr2: 6 <i>c</i> (0.00000, 0.00000, 0.25939)
			Y1: 6 <i>c</i> (0.00000, 0.00000, -0.05355)
			Nb1: 6 <i>c</i> (0.00000, 0.00000, 0.16558)
			Nb2: 3 <i>b</i> (0.00000, 0.00000, 0.50000)
			Al1: 9 <i>e</i> (0.50000, 0.00000, 0.00000)
			B1: 36 <i>i</i> (0.66641, 0.66816, 0.22032)

Similar stability trends are found for the 416 phases, as shown in Figure 4. In total, 12 stable *s*-MAB phases are identified, including 2 with M2 = Sc and 10 with M2 = Y. All of these *s*-MAB phases are dynamically stable (Figures S17-S29). Examples include $\text{Mn}_{4/3}\text{Sc}_{2/3}\text{V}_2\text{AlB}_6$ with $\Delta G_{\text{cp}}^{s\text{-MAB}} = -8$ meV/atom and $\text{Mo}_{4/3}\text{Y}_{2/3}\text{Nb}_2\text{AlB}_6$ with $\Delta G_{\text{cp}}^{s\text{-MAB}} = -6$ meV/atom. The stable *s*-MAB phases mainly include M1 = Cr, Mo, W, Mn, and Fe, combined with M2 = Y and M3 = V, Nb, or Ta. Detailed structural data (space group, lattice parameter, and Wyckoff position) for 416 *s*-MAB phases and its three stackings illustrated in Figure 2 are given in Table S6 with $\text{Mo}_{4/3}\text{Y}_{2/3}\text{Nb}_2\text{AlB}_6$ as a representative case. In addition, 3 partially disordered *s*-MAB phases, all with M2 = Y, and 7 fully disordered MAB phases, 6 with M2 = Sc and 1 with M2 = Y, are also found to be stable. Interestingly, partially disordered *s*-MAB phases are only stable when M2 = Y, while complete disorder of M1, M2, and M3 mainly leads to stable phases when M2 = Sc. More detailed information on stability and the most competing phases is provided in Tables S4 and S5 for M2 = Sc and M2 = Y, respectively.

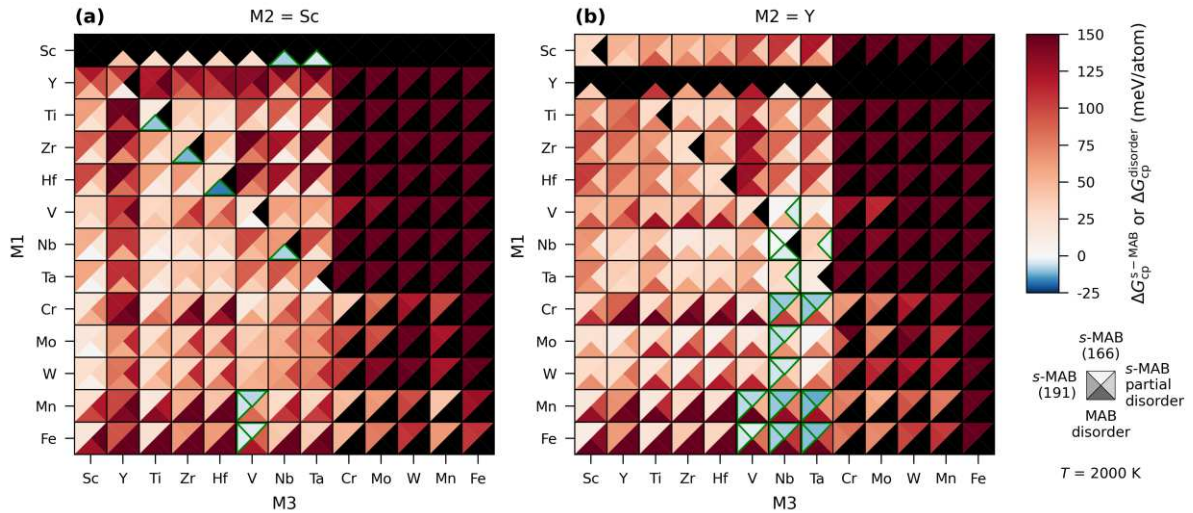


Figure 4. Stability heatmap for hexagonal 416 MAB phases, with configurational entropy included at 2000 K for partially and fully disordered structures and disordered competing phases, upon mixing metals M1, M2, M3 in a 2:1:3 ratio with (a) M2 = Sc and (b) M2 = Y. For a given combination of M1 and M3, the upper and left triangles indicate the stability for combined in- and out-of-plane ordered *s*-MAB, the right triangles indicate the stability for *s*-MAB with partial disorder, having in-plane order of M2 in the outer metal layer combined with disorder of M1 + M3, and the bottom triangles indicate the stability for MAB with disorder of M1, M2, and M3. Stable phases are framed in green. Filled black triangles represent combinations of M1, M2 and M3 not considered.

A summary of the stable *s*-MAB phases predicted in Figure 3 and Figure 4 is given in Table 3, together with their most competing phases. In total, 26 stable *s*-MAB phases are identified. These include 14 phases containing a single M3 layer (Figure 2a-d and Figure 3) and 12 phases containing two M3 layers (Figure 2e-h and Figure 4). The calculated stability of the predicted *s*-MAB phases span $-16 \leq \Delta G_{\text{cp}}^{s\text{-MAB}} < 0$ meV/atom. These modest negative values should not be interpreted as indication of weak intrinsic bonding within the *s*-MAB structures. The quantity $\Delta G_{\text{cp}}^{s\text{-MAB}}$ measures stability relative to the lowest-energy combination of competing phases. Because an *s*-MAB phase contains five elements, its chemical space includes considerably more possible decomposition products than that of a

ternary or quaternary MAB phase. This increases the likelihood of finding a combination of competing phases close in energy to the target structure.

Direct comparison with the stability range of four-element *i*-MAB phases, $-57 \leq \Delta G_{\text{cp}}^{i\text{-MAB}} < 0$ meV/atom (Figure S31), should therefore be made with care. For example, the experimentally synthesized $\text{Mo}_{4/3}\text{Y}_{2/3}\text{AlB}_2$ *i*-MAB phase has $\Delta G_{\text{cp}}^{i\text{-MAB}} = -46$ meV/atom (Figure S31), but it is evaluated in a less compositionally complex chemical space with a different set of competing phases. At the same time, the comparatively small energies calculated for the *s*-MAB candidates indicate relatively modest driving forces against decomposition and should be interpreted within the uncertainties of the computational method and the competing phase dataset. The stability of each candidate is therefore most meaningfully evaluated in relation to its specific set of most competing phases, as listed in Table 3 and Tables S2 to S5.

Despite their modest stability relative to competing phases, the predicted *s*-MAB phases exhibit a substantially stronger energetic preference over the corresponding disordered configurations when evaluating $\Delta G_{\text{cp}}^{s\text{-MAB}} - \Delta G_{\text{cp}}^{\text{partial disorder}}$ and $\Delta G_{\text{cp}}^{s\text{-MAB}} - \Delta G_{\text{cp}}^{\text{disorder}}$. At 2000 K, the ordered structures are favored over the partially disordered models by 29-126 meV/atom and over the completely disordered models by 75-198 meV/atom. Complete disorder is consistently less favorable than partial disorder, demonstrating that the in-plane arrangement of M1 and M2 substantially reduces the energy penalty relative to random mixing of all three metals. Comparable ranges are obtained for the 314 and 416 phases, with no clear indication that either structure type is systematically more susceptible to disorder.

These results indicate that the predicted chemical ordering remains thermodynamically favored even at 2000 K, a temperature selected to emphasize the configurational entropy contribution to the stabilization of disordered compounds. Importantly, stability against decomposition into competing phases and stability with respect to disorder represent distinct criteria where a disordered configuration may be stable relative to competing phases but still remain less favorable than the ordered structure of the same composition. The calculations therefore identify the ordered *s*-MAB structures as the preferred configurations within the present thermodynamic model, although some degree of partial disorder or intermixing may still occur experimentally due to kinetic limitations or incomplete equilibration during synthesis.

It should be noted that all stable *s*-MAB phases in Table 3 have at least one ternary, quaternary, or quinary MAB phase among their most competing phases. For the 314 *s*-MAB compositions, the main competing phases usually include a 416 *s*-MAB phase and an *i*-MAB phase. In contrast, many 416 *s*-MAB phases compete primarily with a combination of 314 *s*-MAB phases and transition-metal diborides, MB_2 . In fact, a 416 *s*-MAB phase can be viewed structurally as a 314 *s*-MAB phase intercalated by an MB_2 layer. This highlights the importance of performing phase stability calculations using as complete a set of competing phases as possible. Such an approach not only gives insight into the strongest competing phases but also helps identify the most promising candidates for experimental synthesis. This is particularly important for *s*-MAB phases, since their calculated stability is strongly influenced by stable competing phases within the five-element chemical space.

Among the predicted candidates, the most promising synthesis targets are those that combine negative $\Delta H_{\text{cp}}^{s\text{-MAB}}$, dynamical stability, and a clear energetic preference over both partially and completely disordered configurations at 2000 K. Based on these criteria, the Y-based compositions with M1 = Cr, Mo, W, Mn, or Fe and M3 = Nb or Ta form the principal candidate group. Nevertheless, their relatively small stability margins against decomposition indicate that the formation of competing phases and the specific synthesis conditions are likely to play important roles in their experimental realization.

Table 3. Predicted stable 314 and 416 *s*-MAB phases and their most competing phases. $\Delta G_{\text{cp}}^{s-\text{MAB}}$ is given for ordered structural models with space groups 191, 194, and 166 where bold values identify the lowest-energy model(s) for each composition. $\Delta G_{\text{cp}}^{s-\text{MAB}} - \Delta G_{\text{cp}}^{\text{partial disorder}}$ and $\Delta G_{\text{cp}}^{s-\text{MAB}} - \Delta G_{\text{cp}}^{\text{disorder}}$ compare the most stable ordered structure with the corresponding partially and completely disordered models, including configurational entropy contributions at 2000 K. Negative values indicate that the ordered *s*-MAB structure is favored. In the partial disorder model, M2 retains its in-plane order in the outer metal layer, whereas M1 and M3 are disordered across the outer and inner metal layers. In the complete disorder model, M1, M2, and M3 are disordered over all metal layers. The final column lists the set of phases identified as the most competitive decomposition reaction where bold text highlight competing MAB phases. Note that $\text{Fe}_{4/3}\text{Sc}_{2/3}\text{VAIB}_4$ is dynamically unstable (Figure S4).

Type	M1	M2	M3	$\Delta G_{\text{cp}}^{s-\text{MAB}}$ (meV/atom)			$\Delta G_{\text{cp}}^{s-\text{MAB}} - \Delta G_{\text{cp}}^{\text{partial disorder}}$ (meV/atom)	$\Delta G_{\text{cp}}^{s-\text{MAB}} - \Delta G_{\text{cp}}^{\text{disorder}}$ (meV/atom)	Set of most competing phases
				191	194	166			
314 MAB	Mn	Sc	V	-2	-3	-3	-58	-110	Mn_{4/3}Sc_{2/3}V₂AlB₆ (416 <i>s</i>-MAB) + Mn_{4/3}Sc_{2/3}AlB₂ (<i>i</i>-MAB)
	Fe	Sc	V	-3	-10	-10	-94	-143	Fe_{4/3}Sc_{2/3}V₂AlB₆ (416 <i>s</i>-MAB) + Fe_{4/3}Sc_{2/3}AlB₂ (<i>i</i>-MAB)
	Cr	Y	Nb	-5	-5	-4	-54	-122	Cr_{4/3}Y_{2/3}Nb₂AlB₆ (416 <i>s</i>-MAB) + Cr₄AlB₄ (414 MAB) + CrYB ₄ + Al ₂ Y + CrB
	Cr	Y	Ta	-11	-10	-10	-54	-128	Ta ₃ B ₄ + Cr _{4/3} Y _{2/3} Ta ₂ AlB ₆ (416 <i>s</i> -MAB) + Cr₄AlB₄ (414 MAB) + CrYB ₄ + Al ₂ Y
	Mo	Y	Nb	-8	-10	-9	-29	-83	Mo_{4/3}Y_{2/3}Nb₂AlB₆ (416 <i>s</i>-MAB) + Mo_{4/3}Y_{2/3}AlB₂ (<i>i</i>-MAB)
	Mo	Y	Ta	-9	-16	-16	-32	-91	Mo_{4/3}Y_{2/3}AlB₂ (<i>i</i>-MAB) + Mo_{4/3}Y_{2/3}Ta₂AlB₆ (416 <i>s</i>-MAB)
	W	Y	Nb	-4	-6	-6	-32	-85	W_{4/3}Y_{2/3}Nb₂AlB₆ (416 <i>s</i>-MAB) + W_{4/3}Y_{2/3}AlB₂ (<i>i</i>-MAB)
	W	Y	Ta	-1	-6	-6	-36	-93	YB ₄ + Al ₃ Y + W _{4/3} Y _{2/3} AlB ₂ (<i>i</i> -MAB) + Al ₅ W + (Ta _{0.5} W _{0.5})B
	Mn	Y	V	1	0	-1	-49	-152	Mn_{4/3}Y_{2/3}V₂AlB₆ + Mn_{4/3}Y_{2/3}AlB₂ (<i>i</i>-MAB)
	Mn	Y	Nb	-8	-8	-9	-86	-147	Mn_{4/3}Y_{2/3}Nb₂AlB₆ (416 <i>s</i>-MAB) + Mn_{4/3}Y_{2/3}AlB₂ (<i>i</i>-MAB)
	Mn	Y	Ta	-14	-14	-15	-87	-157	Mn_{4/3}Y_{2/3}Ta₂AlB₆ (416 <i>s</i>-MAB) + Mn_{4/3}Y_{2/3}AlB₂ (<i>i</i>-MAB)
	Fe	Y	V	-1	-9	-10	-88	-183	Fe_{4/3}Y_{2/3}V₂AlB₆ (416 <i>s</i>-MAB) + Fe_{4/3}Y_{2/3}AlB₂ (<i>i</i>-MAB)
	Fe	Y	Nb	-4	-10	-10	-124	-168	Fe_{4/3}Y_{2/3}Nb₂AlB₆ (416 <i>s</i>-MAB) + Fe_{4/3}Y_{2/3}AlB₂ (<i>i</i>-MAB)
	Fe	Y	Ta	-11	-15	-15	-126	-175	Fe_{4/3}Y_{2/3}Ta₂AlB₆ (416 <i>s</i>-MAB) + Fe_{4/3}Y_{2/3}AlB₂ (<i>i</i>-MAB)
416 MAB	Mn	Sc	V	-5	-8	-7	-64	-93	Mn_{4/3}V_{2/3}AlB₂ (212 <i>i</i>-MAB) + Mn_{4/3}Sc_{2/3}VAIB₄ (314 <i>s</i>-MAB) + (V _{0.75} Sc _{0.25})B ₂
	Fe	Sc	V	-3	1	-3	-91	-126	V ₂ B ₃ + Fe₂VAIB₄ (314 <i>o</i>-MAB) + Fe_{4/3}Sc_{2/3}VAIB₄ (314 <i>s</i>-MAB) + (V _{0.75} Sc _{0.25})B ₂ + Fe ₄ ScAl ₈
	Cr	Y	Nb	-10	-9	-9	-54	-112	Cr_{4/3}Y_{2/3}NbAlB₄ (314 <i>s</i>-MAB) + NbB ₂
	Cr	Y	Ta	-10	-9	-9	-48	-109	Ta ₂ B ₃ + Cr _{4/3} Y _{2/3} TaAlB ₄ (314 <i>s</i> -MAB) + Al + Cr₂Ta₂AlB₆ (416 <i>o</i>-MAB) + CrYB ₄
	Mo	Y	Nb	-6	-5	-6	-34	-75	Mo_{4/3}Y_{2/3}NbAlB₄ (314 <i>s</i>-MAB) + NbB ₂
	W	Y	Nb	-5	-4	-4	-39	-78	W_{4/3}Y_{2/3}NbAlB₄ (314 <i>s</i>-MAB) + NbB ₂
	Mn	Y	V	-7	-8	-7	-58	-168	Mn_{4/3}Y_{2/3}VAIB₄ (314 <i>s</i>-MAB) + VB ₂
	Mn	Y	Nb	-9	-12	-11	-86	-143	Mn_{4/3}Y_{2/3}NbAlB₄ (314 <i>s</i>-MAB) + NbB ₂
	Mn	Y	Ta	-11	-13	-13	-80	-139	Mn_{4/3}Y_{2/3}TaAlB₄ (314 <i>s</i>-MAB) + TaB ₂
	Fe	Y	V	-4	-2	-2	-86	-198	Fe_{4/3}Y_{2/3}VAIB₄ (314 <i>s</i>-MAB) + VB ₂
	Fe	Y	Nb	-8	-8	-8	-115	-171	Fe_{4/3}Y_{2/3}NbAlB₄ (314 <i>s</i>-MAB) + NbB ₂
	Fe	Y	Ta	-10	-8	-11	-110	-170	Fe_{4/3}Y_{2/3}TaAlB₄ (314 <i>s</i>-MAB) + TaB ₂

3.2. Electronic and mechanical properties of selected *i*-MAB and *s*-MAB phases

Figure 5 compares the electronic structure and mechanical properties of the *i*-MAB phase $\text{Cr}_{4/3}\text{Y}_{2/3}\text{AlB}_2$ and the corresponding *s*-MAB phase $\text{Cr}_{4/3}\text{Y}_{2/3}\text{NbAlB}_4$. The *s*-MAB structure can be viewed as an intergrown variant of the *i*-MAB phase, where an additional NbB_2 layer is inserted between the chemically ordered $\text{Cr}_{2/3}\text{Y}_{1/3}$ layers. Both compounds exhibit several electronic bands crossing the Fermi level, shown in Figure 5a,b, together with a pronounced density of states at the Fermi energy. This indicates that both the *i*-MAB and *s*-MAB phases are metallic and should be electrically conducting. The larger number of bands in the *s*-MAB phase reflects its more complex crystal structure and the additional electronic states introduced by the inserted NbB_2 layer. Similar results are found for the Mo- and W-based systems, shown in Figure S39 to S45.

The structural modification from *i*-MAB to *s*-MAB also has a clear effect on the mechanical properties. As shown in Figure 5c-e, the Young's, shear, and bulk moduli of $\text{Cr}_{4/3}\text{Y}_{2/3}\text{NbAlB}_4$ are approximately 20% higher than those of $\text{Cr}_{4/3}\text{Y}_{2/3}\text{AlB}_2$. Similar enhancements are observed for the Mo- and W-based systems, as well as for *s*-MAB with space group no. 191 (Figure S46), indicating that the increased moduli are linked to the *s*-MAB structure. A similar trend is observed across the broader set of compositions shown in Figure 5c-e, where the moduli are compared for *i*-MAB phases with general formula $\text{M}_{14/3}\text{Y}_{2/3}\text{AlB}_2$ and *s*-MAB phases with formula $\text{M}_{14/3}\text{Y}_{2/3}\text{M}_3\text{AlB}_4$, with $\text{M}_1 = \text{Cr, Mo, or W}$ and $\text{M}_3 = \text{Nb or Ta}$. Replacing Nb by Ta in the *s*-MAB phases leads to a slight increase in the calculated moduli, further highlighting the possibility of tailoring properties through targeted compositional design.

The larger calculated moduli of the *s*-MAB compositions can primarily be associated with the thicker metal-boride slab introduced by the additional transition-metal boride M_3B_2 layer. In the *s*-MAB structure, the $\text{M}_{14/3}\text{M}_{2/3}\text{NbB}_4$ block contains two B layers, compared with the single B layer in the $\text{M}_{14/3}\text{M}_{2/3}\text{B}_2$ block of the *i*-MAB phase. Because this comparison changes both structure and composition, it does not isolate the effect of chemical ordering alone. Despite this, the results demonstrate that the structural and compositional degrees of freedom introduced in the predicted *s*-MAB family provide a route for tuning mechanical response.

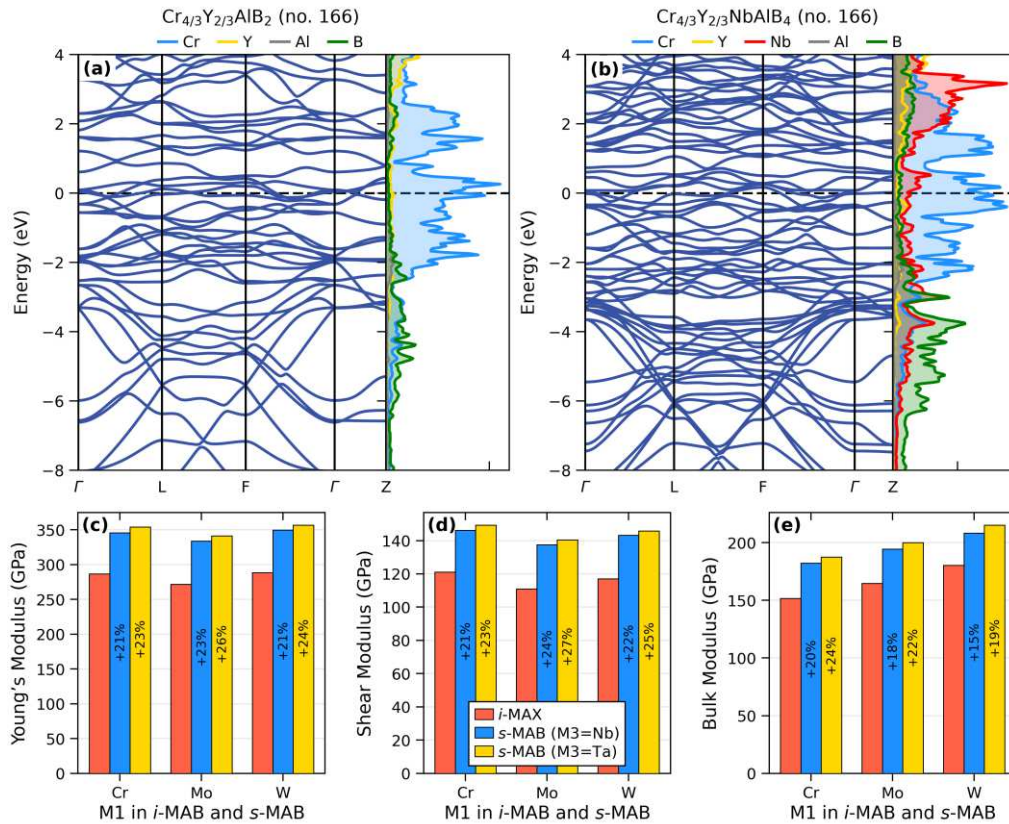


Figure 5. *s*-MAB vs. *i*-MAB. Calculated electronic band-structures and density of states for (a) $\text{Cr}_{4/3}\text{Y}_{2/3}\text{AlB}_2$ *i*-MAB and (b) $\text{Cr}_{4/3}\text{Y}_{2/3}\text{NbAlB}_4$ *s*-MAB, both with space group no. 166. Comparison of (c) Young's, E, (d) shear, G, and (e) bulk, B, modulus for $\text{M}_{14/3}\text{Y}_{2/3}\text{AlB}_2$ *i*-MAB and $\text{M}_{14/3}\text{Y}_{2/3}\text{M}_3\text{AlB}_4$ *s*-MAB phases with percentage change of *s*-MAB relative to *i*-MAB.

3.3. Proof-of-concept synthesis targeting $\text{Cr}_{4/3}\text{Y}_{2/3}\text{NbAlB}_4$ s-MAB phase.

To examine whether the predicted s-MAB motif is experimentally accessible, a proof-of-concept synthesis was performed targeting $\text{Cr}_{4/3}\text{Y}_{2/3}\text{NbAlB}_4$ by solid-state reaction of metal borides (CrB_2 , NbB_2) and elemental powders (Cr, Y, Al). This composition was selected as an experimentally feasible candidate satisfying both the calculated thermodynamic (Figure 3b) and dynamical stability criteria (Figure S6) as well as the large atomic size difference between Cr and Y. The X-ray diffraction (XRD) pattern of the sample with composition $\text{Cr}_{4/3}\text{Y}_{2/3}\text{NbAlB}_4$ is shown in Figure 5a. The peak positions from simulated XRD patterns of the corresponding s-MAB structures (Figure S36) are also shown at the bottom of the figure. The simulated XRD patterns of the three possible structures are very similar, making them difficult to distinguish using XRD alone. The main secondary phase observed in the sample is NbB_2 .

Since all three predicted s-MAB structures of $\text{Cr}_{4/3}\text{Y}_{2/3}\text{NbAlB}_4$ are stable and close in energy, the low-angle peak at 8.3° may be assigned to different out-of-plane reflections depending on the structural model: the (0001) reflection for the no. 191 structure, the (0002) reflection for the no. 194 structure, or the (0003) reflection for the no. 166 structure. Note that we treat the no. 166 structure in its hexagonal representation. The peak at 33.4° corresponds to the (11 $\bar{2}$ 0) reflection for all three structures. Using these peak positions, and considering that the sample may contain a mixture of the three structural variants, the average experimental in-plane lattice parameters were estimated to be $a = 5.352 \text{ \AA}$ and the peak around 8.3° corresponds to a d -spacing of $10.732 \text{ \AA}$. These values are in good agreement with the calculated values listed in Table 2, where $a = 5.35 \text{ \AA}$ and $c = 10.618$, $c/2 = 10.618$, and $c/3 = 10.616 \text{ \AA}$ for the no. 191, 194, and 166 structures, respectively. Note that the no. 194 and 166 structures can be viewed as doubled and tripled variants of the no. 191 structure along the c direction. The difference between the experimental and calculated lattice parameters is $\sim 1\%$, which is within the expected accuracy of PBE. Additional XRD diffractograms obtained for different sintering temperatures, 1350 to 1550°C , and reaction times, 30 to 90 min, are shown in Figures S37 and S38, respectively, indicate that formation of the unidentified layered phase is restricted to a relatively narrow synthesis window around 1375°C and reaction times of up to 60 min.

Energy-dispersive X-ray spectroscopy, EDX, was used to assess the presence and approximate relative abundance of the constituent elements in selected $\text{Cr}_{4/3}\text{Y}_{2/3}\text{NbAlB}_4$ particles. An example EDX spectrum from s-MAB particles is shown in Figure 6b, while the measured compositions in atomic percent are summarized in Table S7. Because light elements such as B are difficult to quantify accurately by EDX, the metal ratios Cr:Y:Nb and the Al content provide a more reliable basis for evaluating the composition. For ideal $\text{Cr}_{4/3}\text{Y}_{2/3}\text{NbAlB}_4$, the expected Cr:Y:Nb ratio is 4:2:3. Four identified particles show compositions close to the expected s-MAB phase. For these particles, the average ratios are Cr/Y = 1.71 compared with the ideal value of 2; Cr/Nb = 1.15 compared with the ideal value of 1.33; (Cr+Y+Nb)/Y = 4.20 compared with the ideal value of 4.5; and (Cr+Y+Nb)/Al = 3.27 compared with the ideal value of 3, as shown in Table S7. The small deviations from the ideal ratios may indicate some degree of Cr/Nb intermixing, which could also contribute to the experimentally observed expansion of the c axis relative to the theoretical value. The results support the coexistence of Cr, Y, Nb, Al, and B in the layered particles but do not independently establish the ideal s-MAB stoichiometry and site occupancies, though the SEM image shown in the inset of Figure 6b reveals the layered morphology expected for $\text{Cr}_{4/3}\text{Y}_{2/3}\text{NbAlB}_4$ particles.

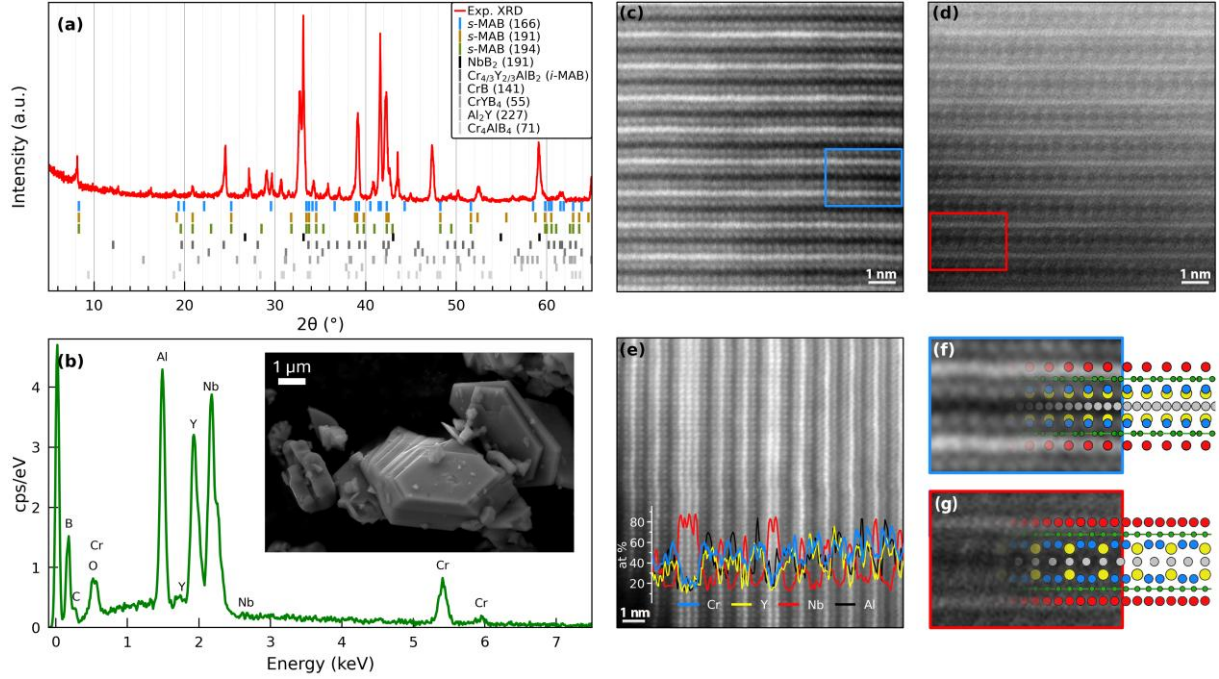


Figure 6. Structural and compositional assessment of a proof-of-concept sample targeting $\text{Cr}_{4/3}\text{Y}_{2/3}\text{NbAlB}_4$ *s*-MAB phase. (a) Measured XRD diffractogram (red) along with theoretical peak positions for three *s*-MAB structures (blue, orange, green) and possible secondary phases such as NbB_2 , $\text{Cr}_{4/3}\text{Y}_{2/3}\text{AlB}_2$, and competing phases from Table 3 (from dark to light grey). (b) EDX spectrum of a $\text{Cr}_{4/3}\text{Y}_{2/3}\text{NbAlB}_4$ particle showing the presence of all constituent elements. Inset shows SEM image of particles assigned to the layered morphology of the candidate *s*-MAB. STEM-HAADF images of $\text{Cr}_{4/3}\text{Y}_{2/3}\text{NbAlB}_4$ *s*-MAB phase along (c) [1-100] and (d) [11-20]. (e) Associated STEM-EDX signals are consistent with alternating Cr/Y-containing and Nb-rich layers. (f,g) Overlay of *s*-MAB schematic and the corresponding atomic arrangements along [1-100] and [11-20] zone axes.

To further support the synthesis of the $\text{Cr}_{4/3}\text{Y}_{2/3}\text{NbAlB}_4$ *s*-MAB, Figure 6 shows STEM-HAADF images viewed along the [1-100] (Figure 6c) and [11-20] directions (Figure 6d). The image along [1-100] shows contrast differences along the *c*-axis, indicative of out-of-plane ordering, however, it is the image along [11-20] that shows the typical *s*-MAB structure expected for space group $R\bar{3}m$, no. 166.

The STEM-EDX signal, Figure 6e, together with the HAADF contrast in Figure 6f,g, provides local contrast and elemental profiles consistent with both ordering motifs in the *s*-MAB structure. In the [1-100] direction, Nb planes, shown in red, are located between mixed Cr and Y planes, shown in blue and yellow. This confirms out-of-plane chemical order for the metal layers. However, in this viewing direction, Cr and Y cannot be clearly separated because they overlap in projection, as shown in Figure 6f. In the [11-20] direction (Figure 6d), Nb and Y atoms are more visible because of their stronger mass contrast. Cr is lighter and therefore less visible, but is located between the Y atoms. This is more clearly seen when the STEM image is overlaid with the structural model in Figure 6g. Together, the STEM-HAADF contrast and STEM-EDX profiles provide local evidence consistent with the coexistence of in-plane Cr/Y ordering and out-of-plane separation of Nb-rich layers in the targeted $\text{Cr}_{4/3}\text{Y}_{2/3}\text{NbAlB}_4$ structure.

4. Conclusion

In this work, we have introduced and investigated super-ordered MAB phases, *s*-MAB, as a new class of layered borides characterized by the simultaneous presence of in-plane and out-of-plane chemical ordering. Inspired by chemical ordering motifs previously established in *i*-MAB, *i*-MAX, *o*-MAX, and *s*-MAX phases, we explored whether comparable structural complexity can be realized within hexagonal MAB-type lattices. Through first-principles phase-stability screening of quinary 314 and 416 compositions, $\text{M}_{14/3}\text{M}_{2/3}\text{M}_3\text{AlB}_4$ and $\text{M}_{14/3}\text{M}_{2/3}\text{M}_3\text{AlB}_6$, we identified 26 *s*-MAB phases

predicted to be thermodynamically stable against the considered competing phases. Most stable candidates have $M2 = Y$ in the in-plane ordered outer metal layer, combined with transition metals from groups 5 to 8 (e.g. Nb, Ta, Cr, Mo, W, Mn) occupying distinct metal sublattices. These trends highlight the importance of combining size-driven in-plane ordering with bonding preferences that favor separation of different transition metals along the stacking direction. The predicted *s*-MAB phases exhibit relatively small negative formation enthalpies, emphasizing the need for a comprehensive stability analysis that includes ternary, quaternary, and quinary MAB phases, transition-metal borides, and chemically disordered configurations as competing phases. In particular, the stability of *s*-MAB phases is strongly influenced by nearby *i*-MAB, *s*-MAB, and MB_2 competing phases. Configurational entropy was included for partially and completely disordered models and disordered competing phases at 2000 K, a temperature selected to emphasize the entropy-driven stabilization upon disorder. Nevertheless, stable fully ordered *s*-MAB structures remain energetically favored over the corresponding partially and completely disordered configurations for every evaluated composition. Electronic-structure and elastic-property calculations show that selected *s*-MAB phases are metallic and possess larger Young's, shear, and bulk moduli than their corresponding *i*-MAB reference phases.

Guided by the theoretical predictions, we performed proof-of-concept synthesis by solid-state synthesis targeting $Cr_{4/3}Y_{2/3}NbAlB_4$. XRD confirms the formation of a layered phase with lattice parameters in close agreement with calculated values, while SEM and EDX verify the presence of particles with the expected layered morphology and near-target metal ratios. Atomic-resolution STEM-HAADF imaging and STEM-EDX mapping provide direct evidence for the key structural feature of the *s*-MAB phases with Nb layers largely separated from Cr/Y-containing layers along the stacking direction and with in-plane chemical ordering of Cr and Y within the outer metal layers adjacent to Al. Hence, these observations support the experimental accessibility of the *s*-MAB phase..

Collectively, these findings identify combined in-plane and out-of-plane ordering as a viable design motif for extending the structural and compositional space of layered borides. The predicted family of stable *s*-MAB phases provides a broad platform for future synthesis and for exploring chemically ordered borides with tunable electronic, mechanical, and chemical properties. Beyond their significance as chemically ordered layered borides, *s*-MAB phases may also act as new precursors for exploring 2D boride-derived materials (boridene/MBene). Although selective etching or exfoliation of *s*-MAB phases remains to be demonstrated, the coexistence of in-plane and out-of-plane chemical order could offer additional opportunities for controlling the composition, ordering, and properties of derived two-dimensional boride structures.

5. Author contributions

M.D. and J.R. conceived the idea and wrote the manuscript. M.D. performed all calculations. R.E. and S.G. performed the synthesis and materials characterization. F.C. and P.P. performed materials characterization. All authors discussed the results and approved the final manuscript.

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7. Competing interests

All authors declare no financial or non-financial competing interests.

8. Data availability

The datasets generated and/or analyzed during the current study are not yet publicly available but are available from the corresponding author on reasonable request.

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