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Synthesis, characterization, and magnetic properties of rare earth containing $\text{Mo}_{4/3}\text{RE}_{2/3}\text{AlB}_2$ -MAB phases

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ABSTRACT

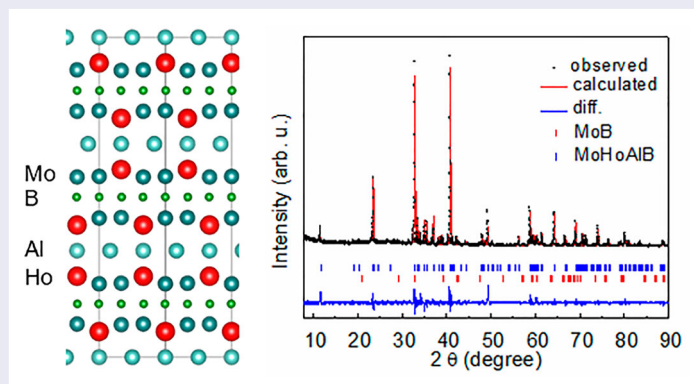
Recently, we presented a family of in-plane chemically ordered transition metal borides of the general formula $(\text{M}'_{2/3}\text{M}''_{1/3})_2\text{AlB}_2$. Here, we investigate incorporation of magnetic rare earth (RE) elements into this structure by synthesis and analysis of $\text{Mo}_{4/3}\text{RE}_{2/3}\text{AlB}_2$, where RE = Ho, Tb, and Er. The crystal structure is verified by X-ray diffraction and scanning transmission electron microscopy, while the composition is derived from energy dispersive X-ray analysis. Through magnetization measurements, we also show that $\text{Mo}_{4/3}\text{Ho}_{2/3}\text{AlB}_2$ orders antiferromagnetically below 9 K. We suggest that $(\text{M}'_{2/3}\text{M}''_{1/3})_2\text{AlB}_2$ could potentially be a versatile platform for new magnetic materials, in 3D as well as 2D.

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Laminated borides; chemical ordering; rare earth elements; magnetic materials



IMPACT STATEMENT

This paper introduces magnetic elements to *i*-MAB phases family with a formula of $\text{Mo}_{4/3}\text{RE}_{2/3}\text{AlB}_2$ (RE = Ho, Er, and Tb), which opens a venue for further exploration of chemically ordered magnetic materials.

Introduction

Binary transition metal carbides and borides (TMCs and TMBs) are well known for their high melting points, high hardness, electrical and thermal conductivities, chemical inertness, as well as magnetic properties [1,2]. By introducing third elements such as Al, they can form atomically laminated structures. One such example is MAX phases [3] ($\text{M}_{n+1}\text{AX}_n$, where M is an early transition metal, A is an A-group element, and X is C and/or N), crystallizing in a hexagonal structure with P63/mmc symmetry, combining the characteristics of metals and

ceramics. The abundant chemistry of these materials renders them promising for applications ranging from structural materials at extreme conditions [3], ohmic contact materials for semiconductors [4], and as precursors for their 2D counterparts, MXenes [5,6]. Another example of atomic laminates is the MAB phases, with larger structural diversity and with one group being given by the general formula of $\text{M}_{n+1}\text{AB}_{2n}$ (where M is a transition metal, A is Al, Zn or Si, and $n = 1-3$), such as MoAlB , WAlB , Fe_2AlB_2 , and Cr_3AlB_4 [7]. MAB phases have shown great potential for many fields, for example, MoAlB has shown

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high-temperature oxidation resistance [8], and especially, Fe_2AlB_2 depicts near-room temperature (304 K) magnetocaloric properties [9]. Moreover, it has recently been shown that MAB phases can serve as precursors for the corresponding 2D solids [10].

Since 2017, we have through alloying expanded the MAX phase family and their attainable properties. We introduced in-plane chemical ordering in MAX phases of the general formula $(\text{M}'_{2/3}, \text{M}''_{1/3})_2\text{AlB}_2$, which we coined *i*-MAX, since the M elements are in-plane ordered [11]. This discovery has greatly expanded the diversity of M elements and their combinations that can be incorporated in the MAX phases structure. This family of in-plane ordered *i*-MAX phases has shown great promise for 2D materials preparation [11] and potentially also for the development of magnetic materials [12,13].

Inspired by the previous discovery of *i*-MAX phases [11], most recently, we theoretically predicted 15 ternary laminated boride phases with in-plane chemical ordering, of the general formula $(\text{M}'_{2/3}\text{M}''_{1/3})_2\text{AlB}_2$ (where M' and M'' are Sc, Y, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Fe, Co, and M' and M'' are in-plane chemically ordered). We called these compounds *i*-MAB phases. The predictions were experimentally verified for $(\text{Mo}_{2/3}\text{Sc}_{1/3})_2\text{AlB}_2$ and $(\text{Mo}_{2/3}\text{Y}_{1/3})_2\text{AlB}_2$ [14].

This structure offers a versatile platform for the potential exploration of magnetic materials, and it is highly motivated to attempt the replacement of Sc and Y with rare earth (RE) elements. We have here synthesized a selection of the corresponding *i*-MAB-phases; $\text{Mo}_{4/3}\text{RE}_{2/3}\text{AlB}_2$, where RE = Ho, Tb, and Er. The synthesis allows further characterization with respect to structure, composition, and magnetic properties, as well as a comparison between structurally and compositionally similar carbides and borides.

Results

Figure 1 shows the scanning transmission electron microscopy (STEM) images of $\text{Mo}_{4/3}\text{Ho}_{2/3}\text{AlB}_2$ along three primary zone axes. The $\text{Mo}_{4/3}\text{Ho}_{2/3}\text{AlB}_2$ *i*-MAB phase crystallizes in a layered morphology resembling that of MAX phase, with typical particle size of a few microns. $\text{Mo}_{4/3}\text{Ho}_{2/3}\text{AlB}_2$ grains obtained after an additional milling step display the typical layered morphology, as shown in Figure 1(a). For the applied imaging conditions, the Mo and Ho atoms appear brightest in the atomic resolution images, the Al atoms are less bright, while B is too light to be visible. The schematics to the side of each micrograph sketch the atomic arrangements assuming hexagonal $\text{Mo}_{4/3}\text{Ho}_{2/3}\text{AlB}_2$ in space group $R\bar{3}m$ (#166). Selective area electron diffraction (SAED)

is shown as an inset for each micrograph. The top view in Figure 1(b) reveals a close-packed hexagonal structure. A cross-sectional image along the $[1\bar{1}00]$ zone axis is shown in Figure 1(c), where Mo and Ho are partially overlapping and thus display an average contrast. However, when viewed from the $[11\bar{2}0]$ zone axis (Figure 1(d)), chemical ordering of Mo and Ho in the M layer is revealed, with the Ho atoms extending from the Mo layer towards the Al layer, a general characteristic of *i*-MAB phases as well as previously studied *i*-MAX phases, and consistent with previous theoretical predictions. Furthermore, the uneven contrast shown within the Al layer is an indication of the formation of a Kagomé lattice, originating from the relaxed A-layer due to the extended Ho atoms.

The X-ray diffraction (XRD) pattern of a sample with a nominal composition of $\text{Mo}_{4/3}\text{Ho}_{2/3}\text{AlB}_2$ is shown in Figure 2(a). Rietveld refinement based on space group $R\bar{3}m$ (#166) is also included in the graph. The detailed refined parameters are shown in Table 1. The lattice parameters calculated from the XRD Rietveld analysis are $a = 5.435 \text{ \AA}$ and $c = 22.647 \text{ \AA}$. The impurity phase MoB is also included in the refinement, which gives a phase composition of 97 wt % $\text{Mo}_{4/3}\text{Ho}_{2/3}\text{AlB}_2$ and 3 wt % MoB. This phase purity is improved when compared to the previously reported $\text{Mo}_{4/3}\text{Y}_{2/3}\text{AlB}_2$ and $\text{Mo}_{4/3}\text{Sc}_{2/3}\text{AlB}_2$ *i*-MAB phases (80% and 62%, respectively). XRD patterns of samples with a nominal composition of $\text{Mo}_{4/3}\text{Er}_{2/3}\text{AlB}_2$ and $\text{Mo}_{4/3}\text{Tb}_{2/3}\text{AlB}_2$ are shown in Figure 2(b), respectively. Due to the limited phase purity of the $\text{Mo}_{4/3}\text{Er}_{2/3}\text{AlB}_2$ and $\text{Mo}_{4/3}\text{Tb}_{2/3}\text{AlB}_2$ samples, we chose to not perform refinement for these materials, and instead, we show the peak position for the *i*-MAB phases. The structural similarity between the three phases shown in Figure 2(b, c) is evident, and all major peaks belonging to the *i*-MAB structure can be identified also for $\text{Mo}_{4/3}\text{Er}_{2/3}\text{AlB}_2$ and $\text{Mo}_{4/3}\text{Tb}_{2/3}\text{AlB}_2$. The main impurity phases are identified as RE_2O_3 and MoB, and the difference in purity may be due to different oxidation tendencies of the rare earth elements. During the synthesis of *i*-MAB phases, secondary phases are usually separated particles. From this point forward, the study will focus primarily on $\text{Mo}_{4/3}\text{Ho}_{2/3}\text{AlB}_2$.

The energy-dispersive X-ray spectroscopy spectrum (EDX) of $\text{Mo}_{4/3}\text{Ho}_{2/3}\text{AlB}_2$, $\text{Mo}_{4/3}\text{Er}_{2/3}\text{AlB}_2$, and $\text{Mo}_{4/3}\text{Tb}_{2/3}\text{AlB}_2$ particles are shown in Figure 3. For the Ho-based sample, the metal atomic ratios of Mo/Ho and $(\text{Mo} + \text{Ho})/\text{Al}$ are 2.0 and 2.0, respectively, consistent with the targeted phase composition of $\text{Mo}_{4/3}\text{Ho}_{2/3}\text{AlB}_2$. Moreover, the Mo:Er and Mo:Tb ratios are in the range of 1.9–2.0, which also confirm the phase composition of $\text{Mo}_{4/3}\text{Er}_{2/3}\text{AlB}_2$ and $\text{Mo}_{4/3}\text{Tb}_{2/3}\text{AlB}_2$, respectively. The

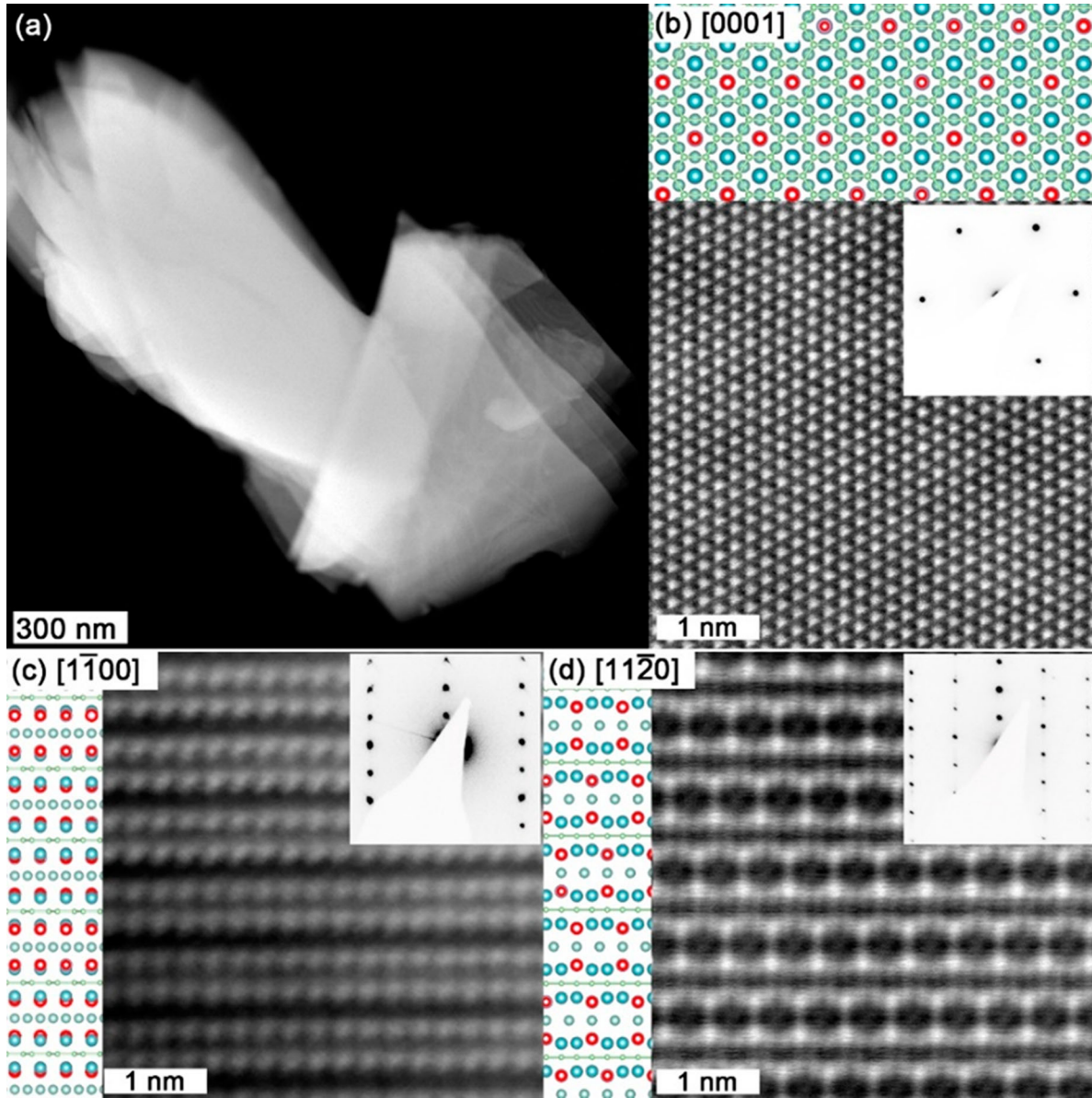


Figure 1. STEM images of $\text{Mo}_{4/3}\text{Ho}_{2/3}\text{AlB}_2$ from three primary zone axes: (a) an overview image of $\text{Mo}_{4/3}\text{Ho}_{2/3}\text{AlB}_2$ particle (the particle represents the fine powder after an additional milling step). (b–d) Atomic resolution image along [0001], [1-100], and [11-20] zone axes with corresponding atomic models, respectively. Insets show their corresponding SAED patterns.

different signal to noise level shown in Figure 3(b) is due to different acquisition times. Figure 4(a) shows the magnetization as a function of temperature. The magnetization follows Curie–Weiss behavior at high temperatures. It shows a sharp anomaly at 9 K, indicating the onset of antiferromagnetic ordering.

Figure 4(b) shows the magnetization as a function of the applied magnetic field. Above the ordering temperature, magnetization is linear to the applied magnetic field. At 2 K, there is a small curvature at ~ 0.2 T, which indicates a spin-flip of an antiferromagnet. The inverse susceptibility obtained from the Arrott plot is shown in Figure 4(c). The inverse susceptibility is fitted to the

Curie–Weiss law as shown below:

$$\chi = C/(T - \theta), \quad (1)$$

where C is the Curie constant and T and θ are the temperature in K and the Curie–Weiss temperature, respectively. From the linear fit, θ is -41 K, indicating a strong antiferromagnetic correlation. The effective moment μ_{eff} per Ho is estimated from

$$C = N\mu_B^2\mu_{\text{eff}}^2/3k_B, \quad (2)$$

where N is the number of magnetic atoms per unit volume, μ_B the Bohr magneton and k_B Boltzmann's

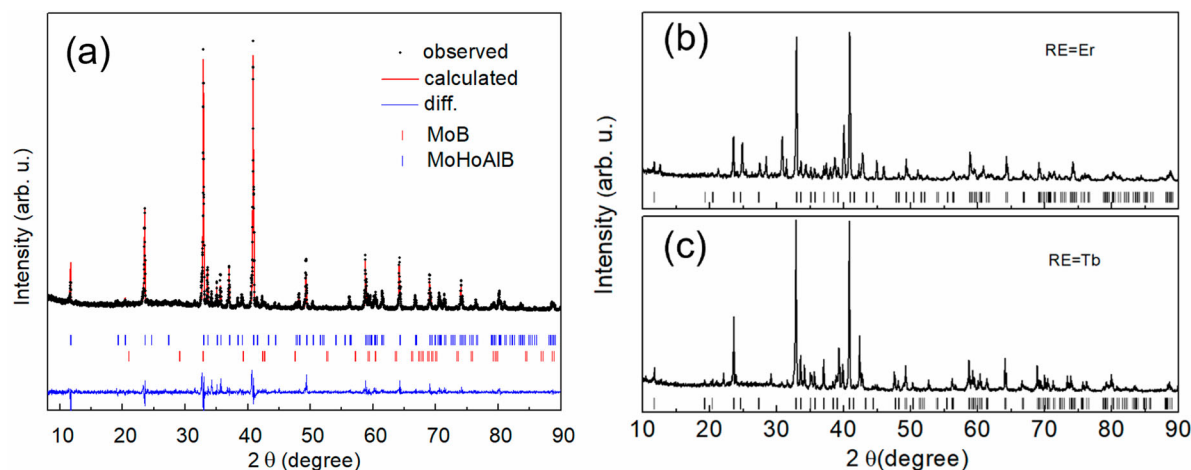


Figure 2. (a) Rietveld refinement of XRD for a sample where the main phase is $\text{Mo}_{4/3}\text{Ho}_{2/3}\text{AlB}_2$. XRD pattern of samples with a nominal composition of (b) $\text{Mo}_{4/3}\text{Er}_{2/3}\text{AlB}_2$ and (c) $\text{Mo}_{4/3}\text{Tb}_{2/3}\text{AlB}_2$. The vertical lines indicate peak positions.

Table 1. Rietveld refinement of the $\text{Mo}_{4/3}\text{Ho}_{2/3}\text{AlB}_2$ *i*-MAB phase ($R_p = 12.7\%$, $\chi^2 = 2.3$).

Formula	$\text{Mo}_{4/3}\text{Ho}_{2/3}\text{AlB}_2$		
Space group	166		
Unit cell	$a = b = 5.435 \text{ \AA}$	$\alpha = \beta = 90^\circ$	
Dimension	$c = 22.644 \text{ \AA}$	$\gamma = 120^\circ$	
Mo1	0, 0, 0.56465 (19)		
Mo2	0, 0, 0.77048 (17)		
Ho	0, 0, 0.91984 (16)		
Al	0.5, 0, 0		
B	0.33906(559), 0, 0.5		

constant. The effective moment is estimated to be $10.06 \mu_B$ per Ho, which is close to the expected value of $10.60 \mu_B$ per Ho from Hund's rule.

Comparing the *i*-MAB phases with *i*-MAX phases, they are structurally closely related. The rare earth elements in the *i*-MAX phases form a distorted 2D triangular lattice, which is sandwiched between Mo carbide layers and Al layers. The rare earth elements in the *i*-MAB structure, on the other hand, form a perfect triangular lattice. From our previous work on *i*-MAX phases, the magnetic frustration is evident [15], which suggests that

rare earth containing *i*-MAB phases could be another platform for exploring the fundamentals of frustrated magnets.

Another promising prospect of the *i*-MAB phases is potential tuning of the electronic structure. Recently, Fe_2AlB_2 was found to display a flat band in the vicinity of the Fermi energy [16], motivating a study of the correlation between the electronic and magnetic structure in *i*-MAB phases.

In conclusion, we have expanded the recently discovered family of in-plane chemically ordered *i*-MAB phases through synthesis of the rare earth containing phases $\text{Mo}_{4/3}\text{RE}_{2/3}\text{AlB}_2$, where RE = Ho, Er, and Tb. We have determined the crystal structure of $\text{Mo}_{4/3}\text{Ho}_{2/3}\text{AlB}_2$ by STEM and XRD, including refinement, verifying the chemical order and a structure belonging to space group $R\bar{3}m$ (#166). XRD analysis of $\text{Mo}_{4/3}\text{Er}_{2/3}\text{AlB}_2$ and $\text{Mo}_{4/3}\text{Tb}_{2/3}\text{AlB}_2$ is also consistent with the same structure, and EDX of all three phases confirms the targeted composition. Characterization of magnetic characteristics shows that $\text{Mo}_{4/3}\text{Ho}_{2/3}\text{AlB}_2$ orders antiferromagnetically below 9 K. The presented addition of magnetic

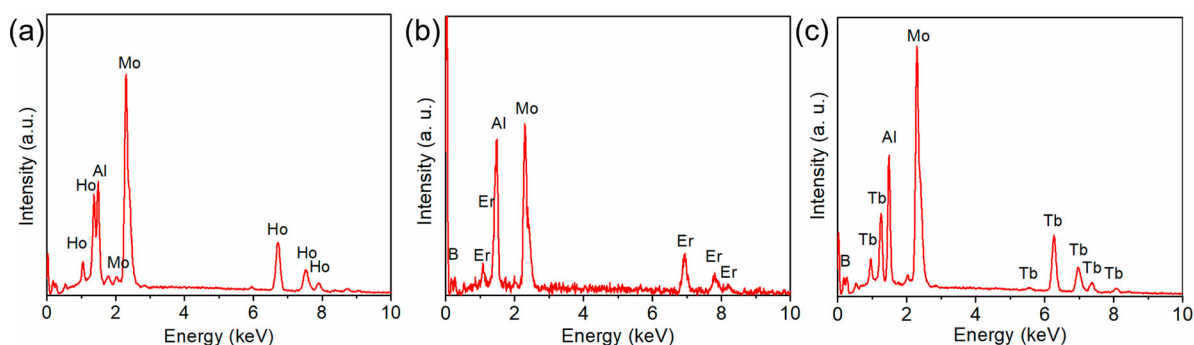


Figure 3. EDX analysis of (a) $\text{Mo}_{4/3}\text{Ho}_{2/3}\text{AlB}_2$, (b) $\text{Mo}_{4/3}\text{Er}_{2/3}\text{AlB}_2$, and (c) $\text{Mo}_{4/3}\text{Tb}_{2/3}\text{AlB}_2$ particles.

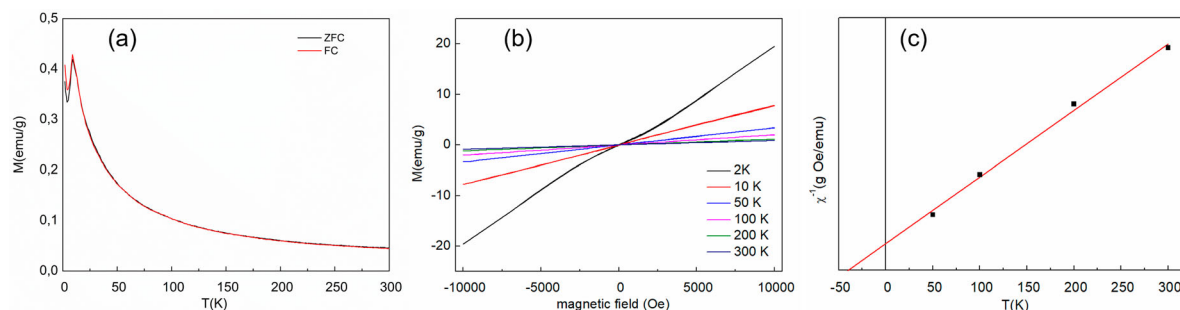


Figure 4. (a) Magnetization vs. temperature. (b) Magnetization vs. applied magnetic field at different temperatures. (c) Inverse susceptibility obtained from Arrott plot and fit the Curie–Weiss law.

elements to the family of *i*-MAB phases opens a venue for further exploration of chemically ordered magnetic materials.

Materials and methods

The powders used herein were B (99.999% Sigma-Aldrich), Mo (99.99% Sigma-Aldrich), Al (99.8% Alfa Aesar), Ho, Er, and Tb (99.99% Stanford Advanced Material). To obtain the $\text{Mo}_{4/3}\text{RE}_{2/3}\text{AlB}_2$ powder samples, a stoichiometric amount was heated to 1400°C in an alumina crucible under flowing argon and held at that temperature for 5 h. After this, the sample was cooled to RT in the furnace and a loosely packed powder was obtained.

XRD scans of $\text{Mo}_{4/3}\text{RE}_{2/3}\text{AlB}_2$ powders were carried out on a diffractometer (Panalytical X'pert) with Cu $K\alpha$ with a step of 0.02 degree. The XRD diffractogram of $\text{Mo}_{4/3}\text{Ho}_{2/3}\text{AlB}_2$ powders was analyzed by the Rietveld refinement method using the FULLPROF code. Refined parameters were the background parameters, zero shift, scale factors, X and Y profile parameters for peak shape, lattice parameters, and atomic positions for all phases. Compositional analysis was carried out using energy-dispersive X-ray spectroscopy (Oxford Instrument) on several $\text{Mo}_{4/3}\text{RE}_{2/3}\text{AlB}_2$ grains (≥ 5), from which the average composition of the grains was obtained. STEM combined with high-angle annular dark-field imaging (STEM-HAADF) and SAED was performed in the double-corrected Linköping FEI Titan³ 60–300 operated at 300 kV. The fine powder was dispersed onto standard holey amorphous carbon support films suspended by Cu grids (SPI Supplies).

The magnetic properties were examined in magnetic fields up to ± 1 T at variable temperatures using a vibrating sample magnetometer (VSM) in a Quantum Design DynaCool Physical Property Measurement System (PPMS).

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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