

## SUPPORTING INFORMATION

### **One-step topochemical transformation of MoAlB into metastable Mo<sub>2</sub>AlB<sub>2</sub> using a metal chloride salt reaction**

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## Experimental Details

### *Chemicals and Materials*

Molybdenum boride powder (MoB, -325 mesh, 99% purity) was purchased from Alfa Aesar. Aluminum chips (Al, 99.99% purity) about 1 mm thick and 12 mm in diameter were purchased from NOAH Technologies. Zinc chloride powder ( $\text{ZnCl}_2$ ,  $\geq 97\%$  purity), lithium chloride powder ( $\text{LiCl}$ ,  $\geq 99.0\%$  purity), and nickel chloride powder ( $\text{NiCl}_2$ , 98% purity) were purchased from Sigma Aldrich. Sodium chloride powder ( $\text{NaCl}$ , GR ACS) was purchased from EMD Millipore Corporation. Quartz wool (fine, fiber size 4-8 microns) was purchased from Chemglass. Crucibles and boats were purchased from CoorsTek.

### *Synthesis of MoAlB Powder*

The MoAlB powder was synthesized according to a previously published procedure.<sup>1</sup> In short, MoAlB was made in 2-g batches by adding molybdenum boride powder and aluminum chips to a 2-mL alumina crucible in a 1:1.3 MoB:Al stoichiometric ratio. The crucible was placed into a mullite tube furnace (Carbolite STF 15/180) under argon flow and heated at 1400 °C for 10 h before being cooled to 900 °C at a rate of 60 °C/h and then quickly cooled to room temperature. The resulting product was processed by grinding with an agate mortar and pestle until a powder resulted.

### *Synthesis of Mo<sub>2</sub>AlB<sub>2</sub>*

MoAlB powder was placed into a porcelain boat and zinc chloride powder was added on top such that the molar ratio of the reactants was 1:10 MoAlB: $\text{ZnCl}_2$ . Anhydrous zinc chloride was weighed in a nitrogen-filled glovebox but had to be removed and exposed to air in order to load it into the boat. During this transition, the  $\text{ZnCl}_2$  unavoidably picks up some water from the air. The boat was placed into a small mullite tube, and the ends of the tube were stuffed with quartz wool to minimize the zinc chloride reacting with the quartz work tube, which would compromise its integrity. The mullite tube was placed into a quartz single-zone tube furnace (Lindberg/Blue Mini-Mite) and heated to 550 °C under nitrogen flow for 170 h. The furnace was turned off and allowed to cool to room temperature before the sample was washed to remove any remaining zinc chloride. This was done by adding Nanopure (18 M $\Omega$ ) deionized water to the product and centrifuging at 14,000 rpm for 2 minutes and resuspending the precipitate two additional times. The sample was then dried by evaporating the water using forced air.

### *Synthesis of Mo<sub>2</sub>AlB<sub>2</sub> using various metal salts*

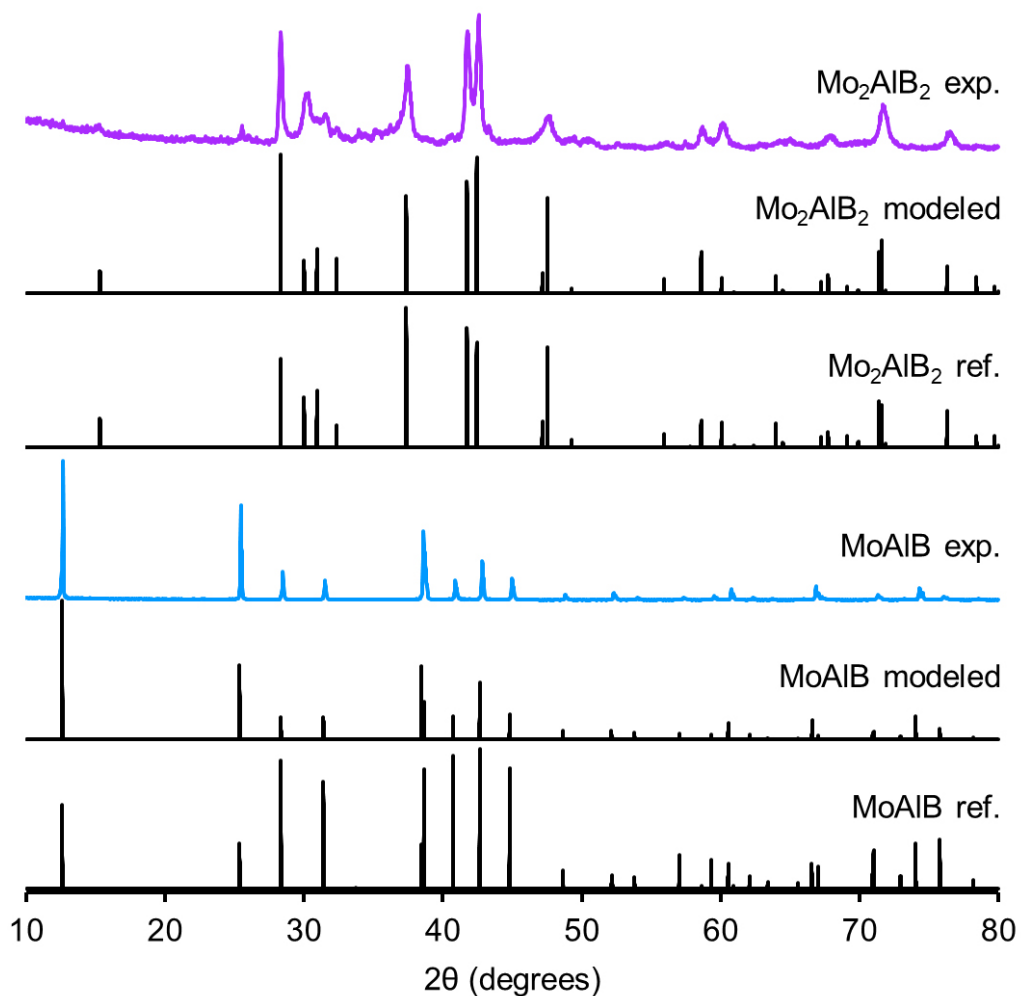
MoAlB powder was placed into a porcelain boat and metal salt ( $\text{MCl}_x$ ) powder was added on top such that the molar ratio of the reactants was 1:10 MoAlB: $\text{MCl}_x$  (note that  $\text{LiCl}$  and  $\text{NiCl}_2$  also picked up some water from the air during transfer). The boat was placed into a quartz single-zone tube furnace (Lindberg/Blue Mini-Mite) and heated to 650 °C under nitrogen flow for 1 h or 36 h, as indicated. The furnace was turned off and allowed to cool to room temperature before the sample was washed with Nanopure (18

M $\Omega$ ) deionized water to remove any remaining metal chloride salt as was described above.

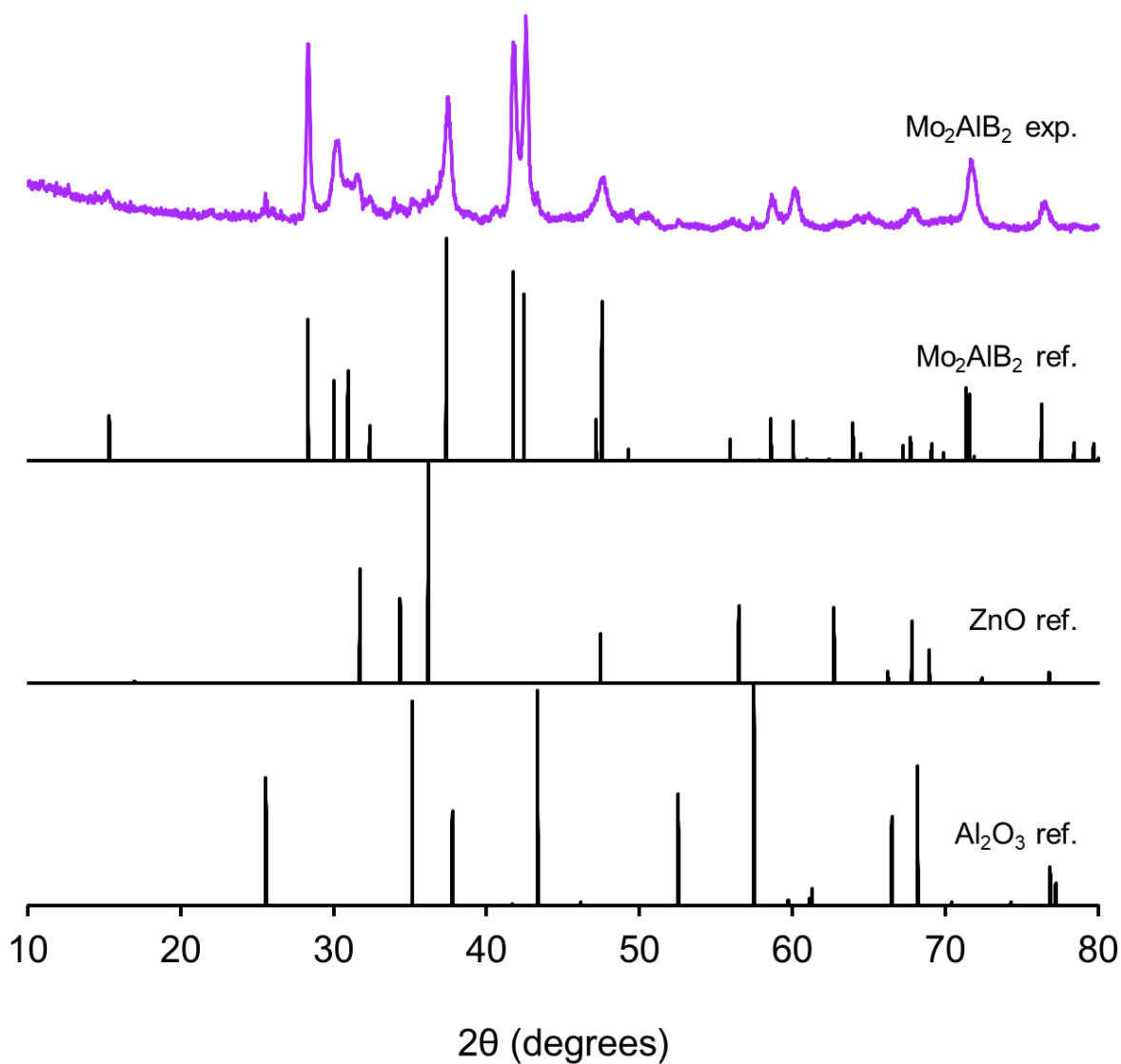
### *Characterization*

Powder X-ray diffraction (XRD) was performed on a Malvern Panalytical Empyrean diffractometer using Cu K $\alpha$  radiation. Reference patterns were simulated using CrystalDiffract<sup>®</sup> software<sup>2</sup> and published crystallographic data for MoAlB<sup>3</sup> and Mo<sub>2</sub>AlB<sub>2</sub>.<sup>1</sup> CrystalMaker<sup>®</sup> software<sup>4</sup> was used to visualize the unit cells of the materials discussed throughout this paper. SEM-EDS was performed on an ESEM Q250 with a tungsten source with a Bruker AXS EDS detector. The ESEM was operated at 20 kV. Samples were pressed into pellets and mounted on carbon tape with the c-axis normal to the stage. Oxford Instruments AZtec software was used to generate SEM-EDS maps and analyze EDS spectra using the L $\alpha$  line for Mo, the K $\alpha$  line for Al, and the K $\alpha$  line for Zn. AZtec was also used for quantification of the EDS data by determining atomic percentages through peak integration.

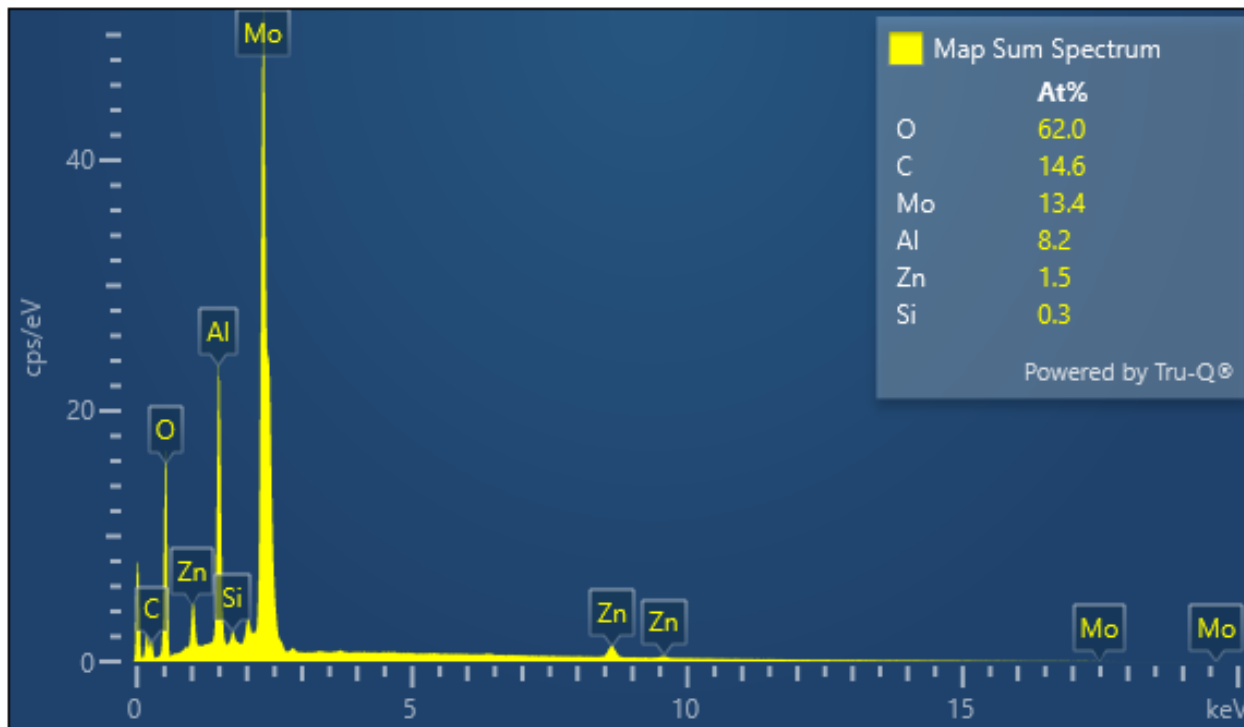
## Additional Characterization



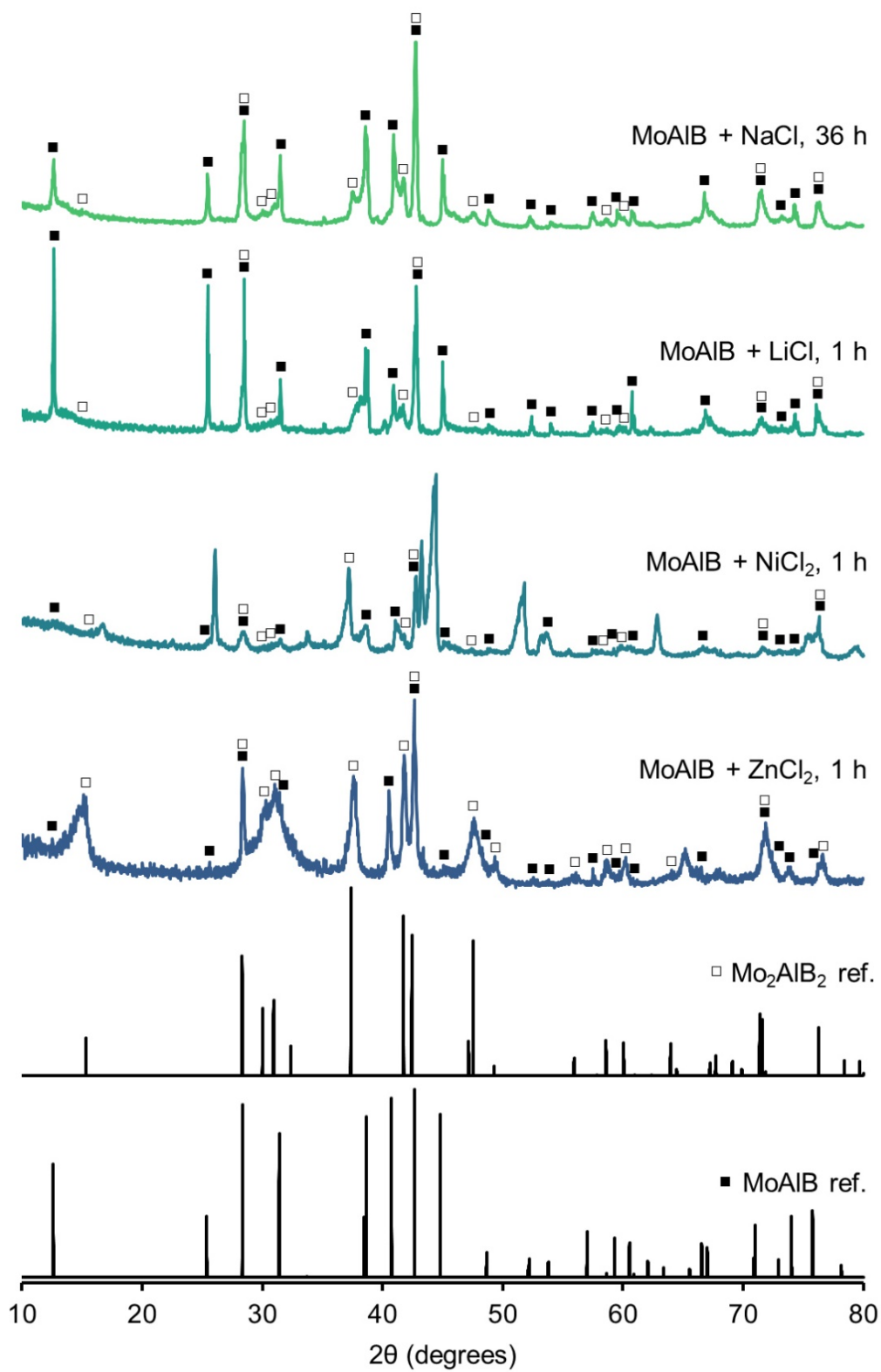
**Figure S1.** Experimental XRD patterns of MoAlB and Mo<sub>2</sub>AlB<sub>2</sub> with as-published reference patterns<sup>1,3</sup> and modeled patterns that account for preferred orientation. MoAlB is modeled with 40% preferred orientation in the 010 and Mo<sub>2</sub>AlB<sub>2</sub> is modeled with 25% preferred orientation in the 021. Using the 021 for Mo<sub>2</sub>AlB<sub>2</sub> captured the observed suppression in *h*00 and enhancement in 020 without causing changes in 00*l*.



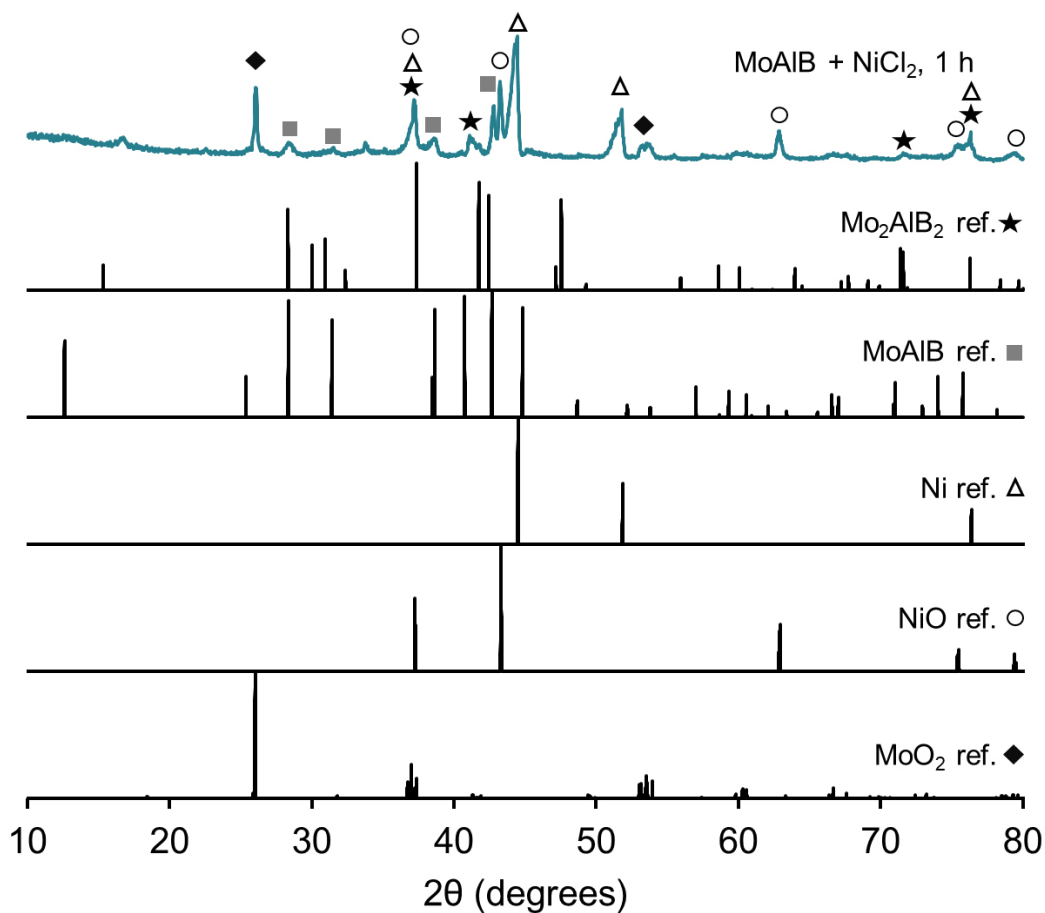
**Figure S2.** Experimental XRD pattern of  $\text{Mo}_2\text{AlB}_2$  as discussed throughout the main text with the  $\text{Mo}_2\text{AlB}_2$  reference pattern<sup>1</sup> along with additional  $\text{ZnO}$ <sup>5</sup> and  $\text{Al}_2\text{O}_3$ <sup>6</sup> reference patterns for comparison.



**Figure S3.** Quantification of the SEM-EDS data corresponding to Figure 3 performed using Oxford Instruments AZtec software which determines atomic percentages through peak integration. Oxygen is expected to largely come from the environment and carbon is from the tape that was used to anchor the sample onto the SEM stub. The small amount of Si is attributed to the reaction vessel.

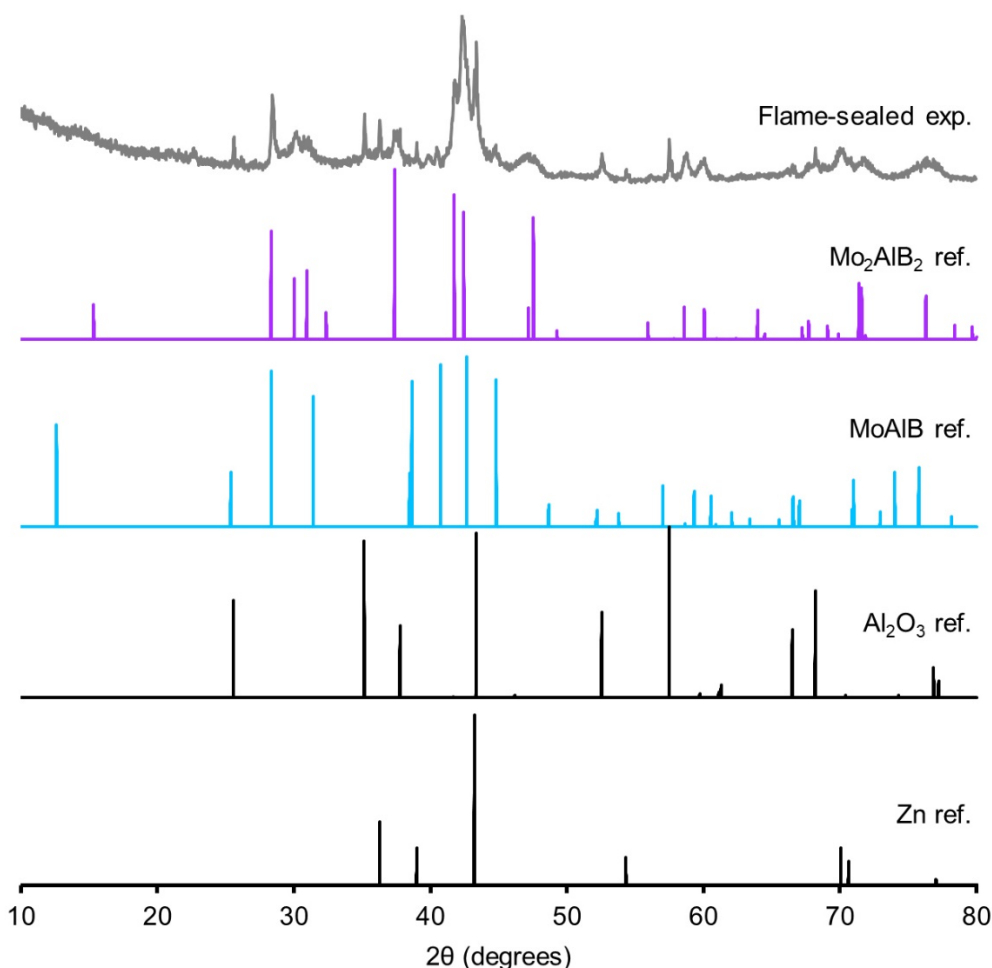


**Figure S4.** An enlarged version of Figure 4 to allow for better visualization of the small peaks that may be difficult to see in the main text.



**Figure S5.** Experimental XRD pattern for the product of the reaction between MoAIB and NiCl<sub>2</sub>, as discussed in the main text, along with the MoAIB<sup>3</sup> and Mo<sub>2</sub>AIB<sub>2</sub><sup>1</sup> reference patterns. Additional reference patterns of Ni<sup>7</sup>, NiO<sup>8</sup>, and MoO<sub>2</sub><sup>9</sup> are provided for comparison. In the experimental patterns, MoAIB peaks are marked by gray squares, Mo<sub>2</sub>AIB<sub>2</sub> by black stars, Ni by white triangles, NiO by white circles, and MoO<sub>2</sub> by black diamonds. Any additional peaks are assumed to be additional decomposition products that cannot be unambiguously identified due to their low intensities and overlap with other peaks.





**Figure S6.** A powder X-ray diffraction pattern for the flame-sealed reaction between MoAlB and ZnCl<sub>2</sub> with references for Mo<sub>2</sub>AlB<sub>2</sub><sup>1</sup>, MoAlB<sup>3</sup>, Al<sub>2</sub>O<sub>3</sub><sup>6</sup>, and Zn<sup>10</sup>. This result shows progression toward Mo<sub>2</sub>AlB<sub>2</sub> while MoAlB character remains validating the necessity of oxygen presence as an oxidizing agent. When less oxygen was present, the reaction proceeded more slowly. Experimental details for this reaction are below.

*Synthesis of flame-sealed reaction of MoAlB and ZnCl<sub>2</sub>*

The quartz tube was coated in carbon to prevent ZnCl<sub>2</sub> from reacting with the tube. The tube and ceramic crucible were dried in a glassware oven at 125 °C overnight. The MoAlB and ZnCl<sub>2</sub> (in 10 times excess) were loaded into the crucible, which was then placed in the quartz tube. This was all done quickly, while the crucible and tube were still hot, to avoid water condensation. The quartz tube was then attached to a vacuum line using flexible plastic tubing. While under active vacuum, the samples were heated to 300 °C, just over the melting point of ZnCl<sub>2</sub>. The materials were held at this temperature for 24 hours to ensure removal of water. The tube was removed and quickly flame sealed, though it was exposed to the atmosphere briefly.

## References:

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