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Final Scientific/Technical Report

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Sponsoring Program Office:	U.S. Department of Energy Energy Efficiency and Renewable Energy
Recipient:	The University of Texas at El Paso Department of Aerospace and Mechanical Engineering 500 W. University Ave., El Paso, TX 79968
Project Title:	Combustion synthesis of nanoscale magnesium borides with improved hydrogen uptake and release
Principal Investigator:	Evgeny Shafirovich
Period of Performance:	March 1, 2023 – December 31, 2025
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Disclaimer

Abstract

The overarching goal of the reported project was to develop reversible metal hydrides that can be dehydrogenated and recharged at relatively low temperatures and pressures. The project complemented the research on reversible metal hydrides for hydrogen storage conducted by the Hydrogen Materials – Advanced Research Consortium (HyMARC). The students involved were trained at both the University of Texas at El Paso (UTEP) and Sandia National Laboratories (SNL). The research objectives were to fabricate nanoscale magnesium boride powders with different B/Mg atomic ratios and to investigate the effects of B/Mg ratio and particle size on the hydrogenation properties of the obtained materials. Magnesium diboride (MgB_2) and tetraboride (MgB_4) were synthesized by using combustion synthesis and by heating in a tube furnace. The latter method resulted in materials with significantly reduced impurity levels. An effective method for the removal of magnesium oxide impurities was identified. High-energy ball milling produced submicron MgB_2 and MgB_4 powders. However, hydrogenation experiments at pressures up to 700 bar have not shown any uptake of hydrogen. Thermogravimetric analysis of the decomposition of the obtained MgB_2 and MgB_4 demonstrated higher thermodynamic stability of the latter. Thus, the boron-rich nature and phase stability of magnesium borides with high B/Mg ratios make them poor candidates for direct hydrogenation. However, the synthesized MgB_4 is a promising energetic additive to solid fuels for high-speed air-breathing propulsion as it offers a lower oxidation onset temperature and greater energy density than MgB_2.

Project Activities

The attempts to fabricate magnesium borides via mechanically activated self-propagating high-temperature synthesis (MASHS) were unsuccessful. However, magnesium diboride (MgB_2), tetraboride (MgB_4), and, in addition, MgB_4-MgB_7 phase were synthesized by using the chemical oven (another variant of combustion synthesis) and by heating in a tube furnace. X-ray diffraction (XRD) analysis has shown that the latter method significantly reduced impurity levels. Since the products still contained noticeable amounts of magnesium oxide, various methods for purification of the obtained borides were tested, and the most effective one was identified. High-energy ball milling produced submicron powders according to scanning electron microscopy (SEM).

At UTEP, hydrogenation of the synthesized MgB_2 was studied by using a high-pressure differential scanning calorimeter (Netzsch DSC 204 HP Phoenix), which, according to the manufacturer, allows for samples to be heated in a hydrogen environment at 150 bar and 450 °C. According to the literature, 120 hours of hydrogenation at these parameters resulted in partial hydrogenation, up to 1 wt% increase in the sample mass (magnesium borohydride contains 14.8 wt% hydrogen). However, it turned out that the cooling system of our instrument did not allow testing at these parameters even for one hour. As a result, tests were conducted at 35 bar, 450 °C and 50 bar, 300 °C for five hours, which was the longest duration allowed. In these experiments, no increase in the sample mass was detected, and XRD analysis confirmed that the crystal structure of MgB_2 remained unchanged.

Hydrogenation of the synthesized MgB_2, MgB_4, and MgB_4-MgB_7 phases was tested at 700 bar and 300 °C for 48 hours in a custom-made high-pressure hydrogen system at Sandia National Laboratories – Livermore. Figure 1 shows the XRD patterns of the tested samples. The powders were tested in their bulk synthesized state as well as after being activated by ball milling for 2 and 4 hours.

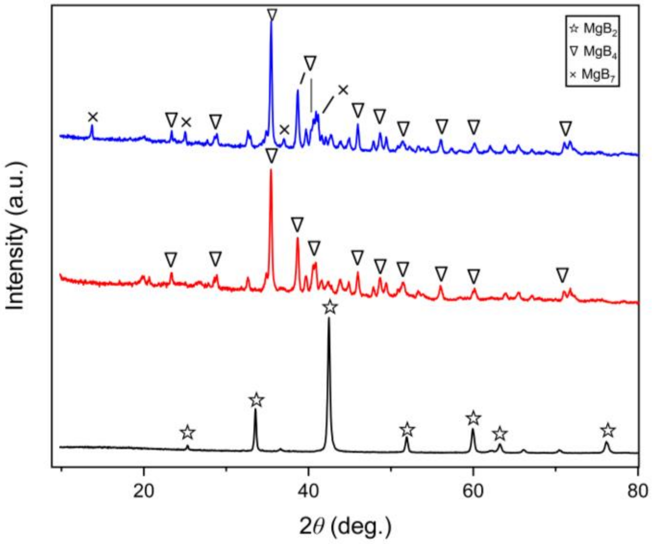

Fig. 1. XRD patterns of MgB_2 (bottom), MgB_4 (middle), and MgB_4-MgB_7 (top).

Samples were loaded into stainless-steel crucibles with a frit and retaining ring to contain individual samples inside a glovebox (<0.1 ppm O_2, <0.1 ppm H_2O). The samples were then loaded into the high-pressure hydrogen system. After hydrogenation experiments, the samples were examined with FTIR spectroscopy and XRD analysis to probe whether a reaction had occurred. Figure 2 shows the obtained infrared absorbance spectra of reference MgB_2 and $Mg(BH_4)_2$, of powders hydrogenated in their bulk synthesized state, and of powders hydrogenated after 4 hours of activation by ball milling. These spectra show that no reaction occurred in any of the powders.

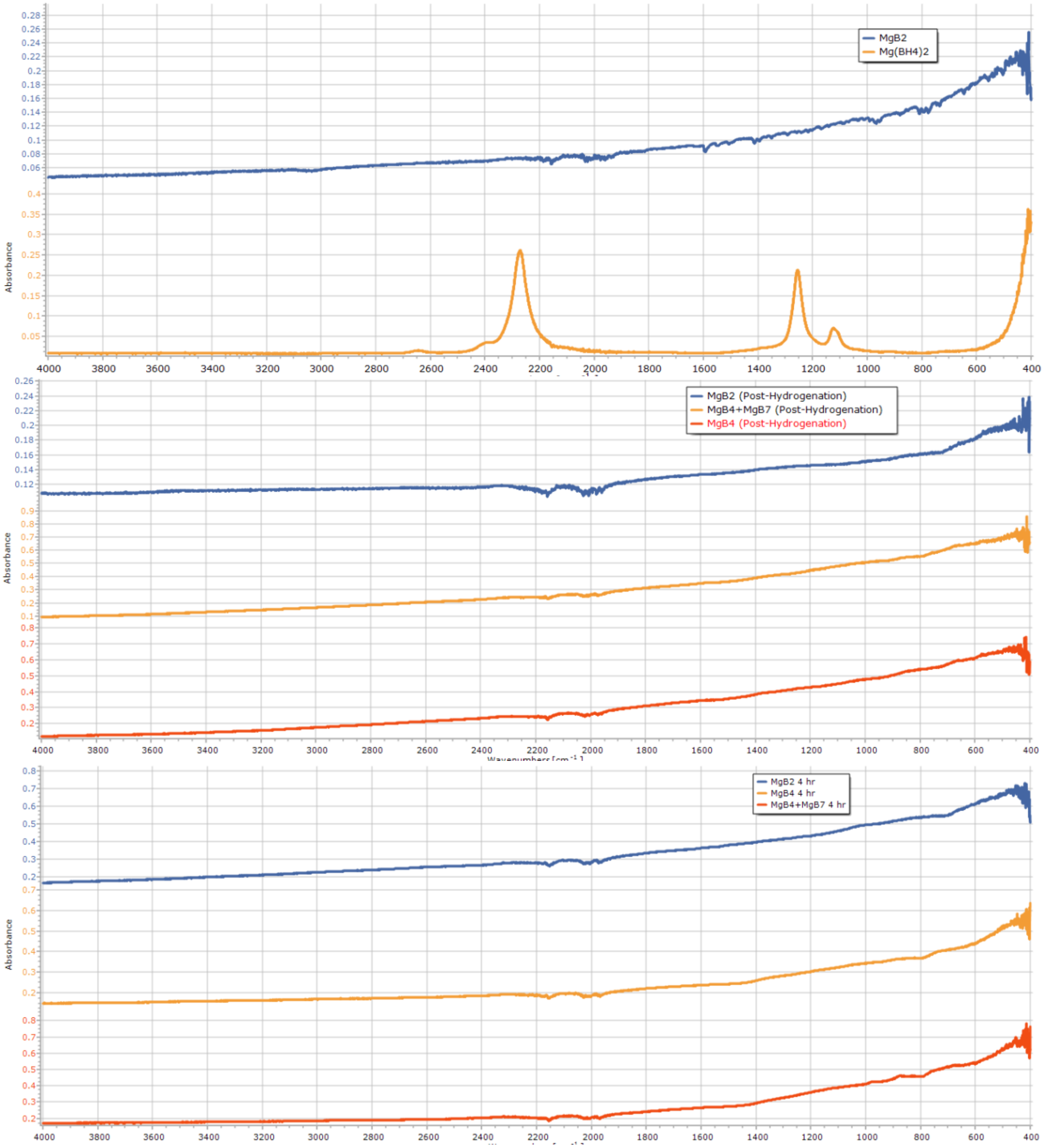

Fig. 2. The IR absorbance spectra of reference MgB_2 and $Mg(BH_4)_2$ (top), powders hydrogenated in their bulk synthesized state (middle), and powders hydrogenated after 4 hours of activation by ball milling (bottom).

For XRD analysis, samples that had undergone hydrogenation testing were loaded into capillary tubes as a safety precaution. Figure 3 shows the XRD patterns of MgB_2 before and after the hydrogenation procedure. It is seen that the crystal structure remains unaltered (MgB_2 peaks are dominant in both patterns with no $Mg(BH_4)_2$ peaks after the hydrogenation procedure).

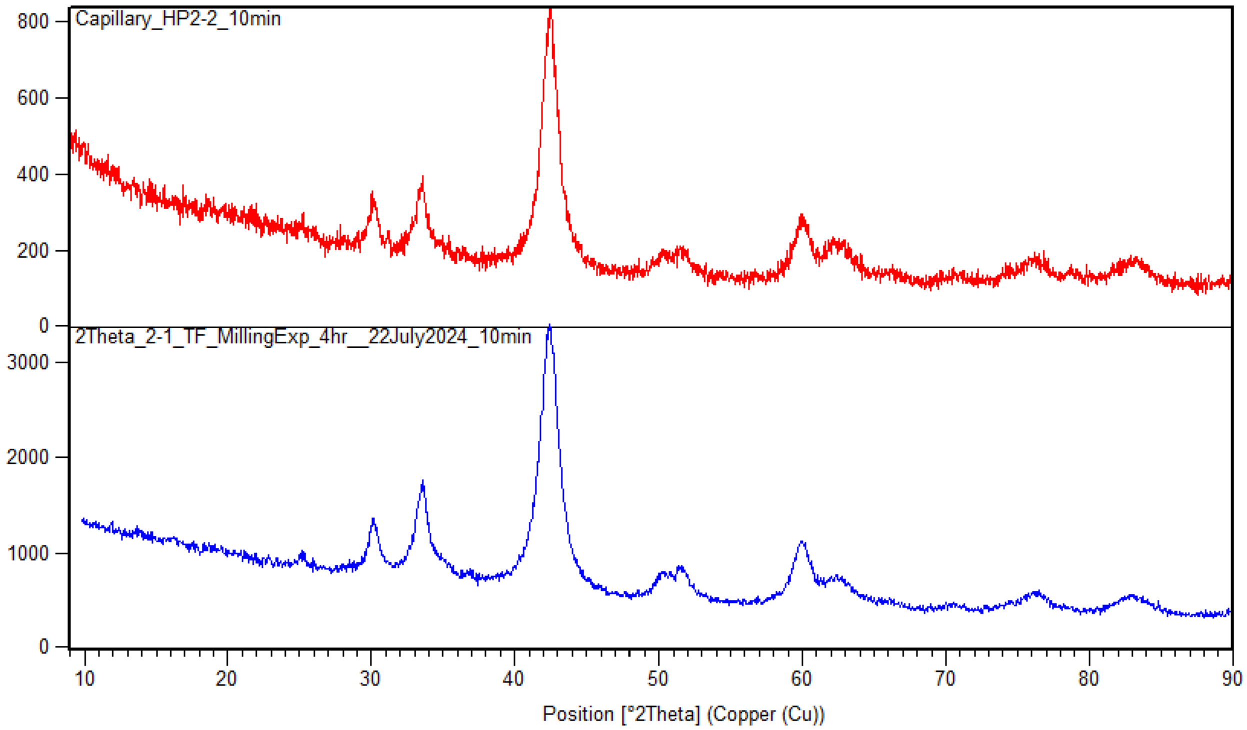

Fig. 3. XRD of milled MgB_2 before (bottom) and after (top) hydrogenation procedure.

Based on the testing at SNL, we suggest that borides with greater concentrations of boron do not yield any significant improvement in hydrogenation over MgB_2.

To understand why the obtained magnesium borides did not absorb hydrogen, we have conducted thermogravimetric analysis (TGA) of MgB_2 and MgB_4 decomposition. The observed decomposition pathway includes several steps and the formation of intermediate MgB_7 and MgB_{20} phases. This indicates a high thermodynamic stability of the boron-rich phases and suggests that significant structural rearrangement is required before hydrogen can be effectively incorporated. The observed stability of MgB_4 until very high temperatures (over 1000 °C) reinforces the idea that the boron-rich nature and phase stability of magnesium borides with B/Mg ratios over two make them poor candidates for direct hydrogenation.

While the performed experiments did not confirm the expectations of improved hydrogen intake by magnesium borides with high B/Mg ratios, such as MgB_4, it was realized that these materials are promising energetic additives to solid fuels for high-speed air-breathing propulsion systems such as solid fuel ramjets. TGA of their oxidation indicated that MgB_4 exhibits a lower reaction onset temperature than MgB_2, while offering greater energy density than MgB_2 and achieving a higher extent of conversion than submicron amorphous boron. Combustion experiments with thin layers of powders have shown that the synthesized magnesium borides MgB_2 and MgB_4 burn much faster than submicron boron. High-energy ball milling further accelerates their combustion. The gained insights into the combustion of magnesium borides will help fully utilize the great potential of boron as fuel for supersonic/hypersonic air-breathing propulsion.

Detailed scientific and technical information (STI) obtained in this project is publicly accessible via a journal article and an M.S. thesis:

Camarena, M.J., “Optimization and purification of magnesium borides fabricated by combustion synthesis and by high-temperature sintering,” M.S. Thesis, The University of Texas at El Paso, El Paso, TX, 2024, OSTI ID #3011733

Abstract: Hydrogen as a fuel provides several benefits over the use of fossil fuels; however, one challenge in utilizing hydrogen as an energy carrier revolves around its storage. Achieving sufficient volumetric hydrogen density in a storage solution will facilitate hydrogen’s adoption for use in both stationery and mobile applications. Solid-state hydrogen storage provides a promising pathway to solving this problem. However, the hydrogenation of these materials is characterized by slow kinetics and extreme thermodynamic conditions. Magnesium borohydride ($Mg(BH_4)_2$) is a promising material in hydrogen storage due to its reversible properties and a theoretical hydrogen capacity of 14.9 wt.%. To synthesize this material, combustion synthesis of magnesium borides (MgB_x) has been implemented with the aim of further lowering thermodynamic requirements for direct hydrogenation. A drawback of this process is the potential formation of oxide contaminants, which decrease hydrogenation/dehydrogenation and recyclability performance. The present work focuses on identifying parameters useful for reducing contamination and evaluating potential pathways to the purification of magnesium borides with the goal of improving their quality.

Molina, A., Camarena, M.J., and Shafirovich, E., “Fabrication, oxidation, and combustion of nanoscale magnesium diboride and tetraboride,” *Combustion and Flame* 285 (2026) 114759, https://doi.org/10.1016/j.combustflame.2025.114759, OSTI ID #3011732

Abstract: The difficult ignition and low combustion efficiency of boron particles decrease the performance of boron-loaded, fuel-rich propellants for solid fuel ramjets and ducted rockets. One approach to solving this problem involves the use of magnesium diboride (MgB_2), which ignites easier than boron. Magnesium tetraboride (MgB_4) offers greater energy density owing to its higher boron content. However, the effect of B/Mg ratio on the ignition and combustion is unknown. Additionally, while nanoscale MgB_2 particles and quasi-2D structures are promising energetic additives, the oxidation and combustion properties of nanoscale MgB_4 have not been explored. To address these knowledge gaps, the present work included synthesis and high-energy ball milling of MgB_2 and MgB_4 powders, thermogravimetric analysis (TGA) of their oxidation, and combustion experiments with thin layers of the obtained powders. Comparison of two synthesis routes (a solid-state reaction in a tube furnace and combustion synthesis) has shown that the former is the superior method for producing magnesium borides. TGA has revealed that oxidation of both MgB_2 and MgB_4 results in a high conversion into the oxides (88-91%), far exceeding the low conversion of boron (62.5%). MgB_4 begins to oxidize rapidly at a much lower temperature (~900 °C) than MgB_2 (~1200 °C). The burning rates of milled MgB_2 and MgB_4 are about eight and five times, respectively, faster than that of submicron boron. Magnesium borides exhibit a stable, sustained boron flame, needed for high combustion efficiency, whereas physical Mg/B mixtures undergo Mg-driven "flash" combustion.

The STI was also presented to the scientific community at the following meetings:

- DOE Hydrogen Program 2024 Annual Merit Review and Peer Evaluation Meeting, May 6 – 9, 2024, OSTI ID #3012120

- 14th U.S. National Combustion Meeting, March 16-19, 2025, Boston, MA, OSTI ID #3011757
- 15th International Workshop on Combustion and Propulsion (IWCP), July 6-9, 2025, Pescara, Italy, OSTI ID #3011758

One PhD student (Andre Molina) and one master's student (Miguel Camarena) have worked on the project. Camarena was trained at Sandia National Laboratories – Livermore from June 12 to August 4, 2023, and Molina was trained there from June 13 to August 9, 2024.