

X-ray Diffraction on Lightweight Materials for Hydrogen Storage

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Introduction

To further investigate the final products after exposing MgB_2 , TiB_2 , CaB_6 , AlB_2 , AlB_{12} , B_{13}P_2 , and B_4C to H_2 at high temperature, high resolution x-ray diffraction experiments were conducted at the APS/MRCAT (Sector 10). The results of these experiments are summarized in this report.

Methods and Materials

A ThermoCahn Model TG-2121 thermogravimetric analyzer (TGA) was used. The instrument has a sensitivity of $0.1\mu\text{g}$. The empty quartz basket was tared in argon prior to loading the sample. Hydrogen (AGA Gas, ultra high purity, 99.999%) and argon (AGA Gas, ultra high purity, 99.999%) were used. Each gas supply line was equipped with a No. 8123 In-Line Moisture Trap (Alltech, efficiency < 1ppm) followed by a No. 4004 Indicating Oxy-Trap (Alltech, efficiency < 1ppb). Flow rates of the gases were 50 mL/min determined with a Fisher Model 520 electronic bubble flowmeter. Samples were purged with argon for 60 minutes prior to introducing hydrogen. Samples were then purged with H_2 for 90 minutes prior to heating the samples. Samples were kept under the reaction gas during the heating/cooling cycles. Heating rates were $5^\circ\text{C}/\text{min}$ and cooling rates were $10^\circ\text{C}/\text{min}$ unless indicated otherwise.

X-ray diffraction measurements we made on the samples loaded in 0.5mm – 1.0 mm glass capillaries. The capillaries were spun at several hundred rpm. The x-ray wavelength was $1.2398(1)\text{ \AA}$ and a double slit collimator was used in front of the detector, achieving a 2θ resolution of 0.065° .

Results

Figure 1 depicts the results of holding AlB_2 at 600°C for 12 hrs under H_2 . As can be seen the weight of the sample continues to increase over during the 12 hr duration. A second experiment was conducted at temperatures of 600°C , 800°C , and 900°C the results of which are shown in Figure 2. Again, the weight of the sample of AlB_2 continued to increase with faster rates at higher temperatures. The high-resolution XRD data showed the resulting products of the AlB_2 experiment were Al_2O_3 and B_2O_3 oxides. Table 1 summarizes the expected weight increases assuming two different reactions that would lead to the products observed by the XRD experiments.

Clearly, the mass differences observed for the AlB_2 sample after H_2 treatment for longer reaction times either surpass or fall well below those expected based on the proposed reactions listed in Table 1. As both Al_2O_3 and B_2O_3 were observed in XRD data it is expected that the first reaction of Table 1 is the most probable.

Efforts to characterize the samples, before and after exposure to H_2 , using far infrared (far-IR) spectroscopy experiments yielded little or no information. High resolution XRD experiments were then conducted at the MRCAT at the APS. Figure 3 demonstrates the quality of the data obtained at the MRCAT versus data that was collected using a laboratory instrument. Without the high-resolution data it is very difficult

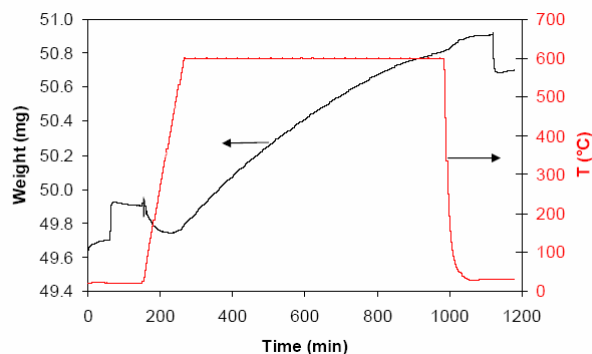


Figure 1. TGA trace of AlB_2 at 600°C for 12 hrs under H_2 .

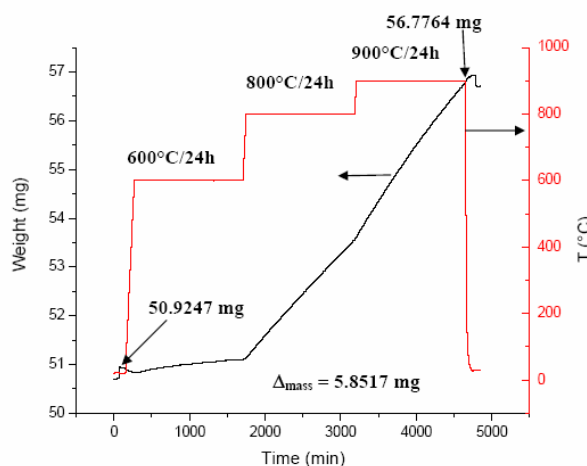


Figure 2. TGA trace of AlB_2 under H_2 for 24 hrs at temperatures of 600°C , 800°C , and 900°C .

to assign the proper phase to the AlB_{12} sample, $\alpha\text{-AlB}_{12}$ vs. $\beta\text{-AlB}_{12}$. Of the samples tested only the AlB_2 and MgB_2 samples demonstrated significant changes in their XRD patterns after treatment in H_2 up to 1000°C . All of the samples were compared to the available Powder Diffraction File (PDF) cards. The AlB_2 purchased from Aldrich has a small amount of aluminum metal present (Figure 4). After five cycles of 30-1000-30 $^\circ\text{C}$ under H_2 the peaks corresponding to Al metal increase significantly with a concomitant decrease in the AlB_2 peaks. These observations suggest that an overall decrease in weight should be observed if boron is removed from the sample. However, even after five cycles small, but observable, peaks corresponding to Al_2O_3 and B_2O_3 can be observed in the XRD traces. After ten cycles the Al_2O_3 peaks increase in intensity corresponding to the continuous increase in weight observed during the TGA experiments. An important result from the TGA experiments is that AlB_2 is stable, with a slight weight loss, at temperatures up to 500°C . Above 500°C AlB_2 begins to react with the trace O_2 present in the gas stream. AlB_2 still

Table 1. Expected weight changes based on the reaction of AlB_2 with O_2 and H_2 during the H_2 TGA experiments.

	FW	Mass (mg)	mmoles
$2\text{AlB}_2 + 4.5\text{O}_2 = \text{Al}_2\text{O}_3 + 2\text{B}_2\text{O}_3$			
AlB_2	48.6015	50.0000	1.0288
O_2	31.9988	74.0690	2.3147
Al_2O_3	101.9613	52.4476	0.5144
B_2O_3	69.6182	71.6215	1.0288
Mass difference		74.0691	
$2\text{AlB}_2 + 6\text{H}_2 + 1.5\text{O}_2 = \text{Al}_2\text{O}_3 + 2\text{B}_2\text{H}_6$			
AlB_2	48.6015	50.0000	1.0288
H_2	2.0158	6.2214	3.0863
O_2	31.9988	24.6897	0.7716
Al_2O_3	101.9613	52.4476	0.5144
B_2H_6	27.6674	28.4635	1.0288
Mass difference		2.4476	

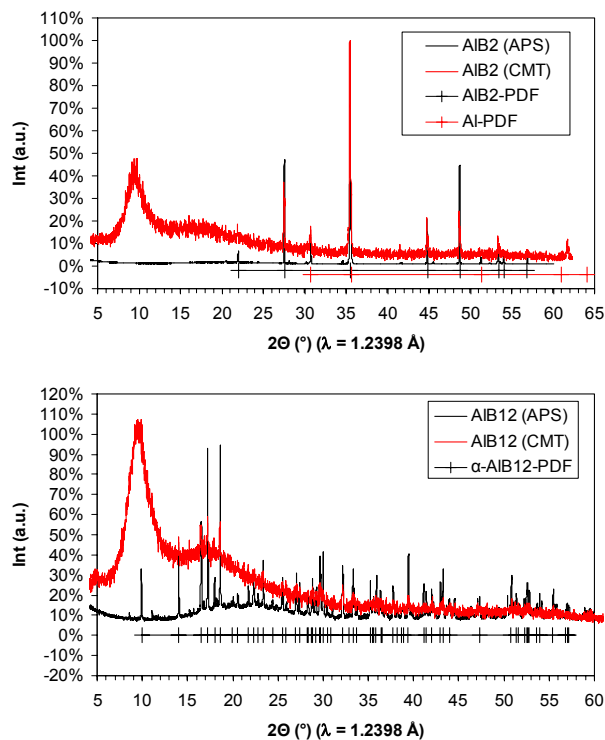


Figure 3. Comparison of the XRD traces collected on laboratory x-ray diffractometer and the APS. The residual Al metal, in the AlB_2 sample, is more clearly seen in the high-resolution APS data. The assignment of α -phase to the AlB_{12} sample is straight forward.

holds promise as a potential hydrogen storage material that may demonstrate a tolerance to trace contaminants present in the source hydrogen.

The MgB_2 sample had demonstrated a very large weight loss at $\sim 900^\circ\text{C}$ under a stream of H_2 . The interior surface of the quartz reactor tube became coated with the product of decomposition. As a slight excess of boron was initially present, it was thought

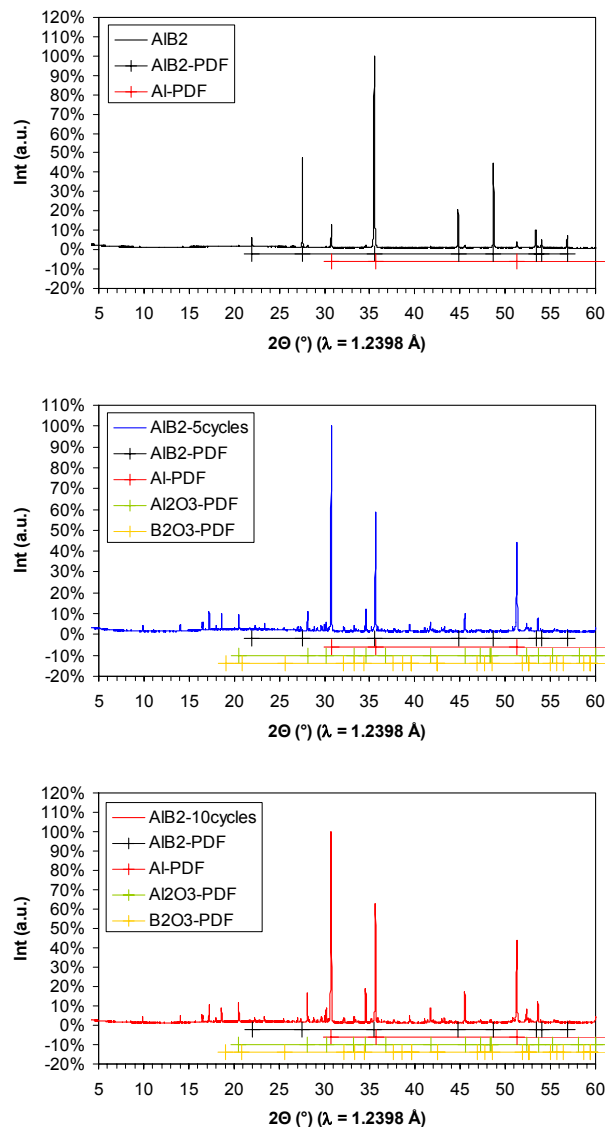


Figure 4. XRD traces of AlB_2 before and after 5-cycles and 10-cycles of $30\text{-}1000\text{-}30^\circ\text{C}$ in 99.999% H_2 . The peaks due to Al metal and Al_2O_3 increase with increasing number of cycles.

that the product was decomposed diborane. These experiments clearly showed that the MgB_2 sample is converted to MgO . Elemental analysis has not been performed on the treated sample, but from the XRD trace (not shown) it appears that all of the MgB_2 is converted to MgO with residual elemental boron present.

For the other samples tested there were no significant changes in structure or composition after treatment in H_2 up to 1000°C . The TiB_2 sample is nearly identical before and after treatment in H_2 . The CaB_6 sample also seems unaffected by treatment in H_2 . Several of the peaks for CaO overlap with those for CaB_6 , thus making it difficult to discern if any CaO was actually formed. The formation of CaO is unlikely since the weight of the CaB_6 sample begins to level off at the end of the second temperature cycle under H_2 .

Acknowledgments

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