Production and Doping of Superconducting Material MgB_2

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Abstract

Magnesium and Boron were mixed at different stoichiometries and exposed to different heat treatments in order to find the best production method of MgB_2 in a flowing Argon furnace under atmospheric pressure. X-ray diffraction was used to determine the purest sample. The Magnesium and Boron were doped with Vanadium, Niobium, and Titanium according to the stoichiometry $Mg_{1.2-x}A_xB_2$, where x = 0.05, 0.1, 0.15, and 0.2. Two different heat treatments were used on each doped sample. X-ray diffraction was used to analyze the doped samples and the most promising were measured on the SQUID magnetometer to find their superconducting and magnetic properties. Vanadium showed some promising results.

Introduction

The discovery of superconductivity in Magnesium Diboride at 39K[1] has lead to great excitement in the scientific community. Magnesium Diboride, despite its relatively low Tc compared to ceramic superconductors, has great advantages, such as inexpensive and simple production. It has been found that the grain boundaries in MgB_2 help to pin magnetic flux rather than impede it[2]. Some dopants such as Titanium can lie within the grain boundaries, further improving properties such as J_c and H_c[3]. This discovery motivated the testing of similar dopants Vanadium and Niobium.

Methods and Materials

Production of Pure MgB_2

Magnesium and Boron powders were weighed in the atomic ratios of 1:2, 1.1:2, 1.2:2, and 1.3:2. The powders were mixed in a marble mortar and pestle for approximately 15 minutes and then pressed into 1g pellets using 2 metric tons. The pellets were placed into small boxes (1cm edge) made from .125 mm Nickel foil to help control Magnesium evaporation. The pellets were placed in an Alumina boat and heat-treated in a calibrated cylindrical furnace with flowing Argon. Four pellets were used in each heat-treatment in order to keep the level of Magnesium vapor pressure constant. Seven different heat treatments were examined to find which gave the purest form of MgB_2. The treatments are as follows:

	Rate 1	Temp	Dwell	Rate 2	Temp	Dwell	Rate 3	Temp	Dwell	Rate4	Temp
1	400°/hr	600°C	1 hr.	400°/hr	800°C	1 hr.	400°/hr	900°C	1 hr.	Step	Room
2	Step	600°C	1 hr.	Step	800°C	1 hr.	Step	900°C	1 hr.	Step	Room
3	400°/hr	600°C	1 hr.	400°/hr	800°C	1 hr.	400°/hr	900°C	1 hr.	400°/hr	Room
4	Step	600°C	1 hr.	Step	800°C	1 hr.	Step	900°C	2 hrs.	Step	Room
5	Step	600°C	1 hr.	Step	800°C	1 hr.	Step	900°C	2 hrs.	400°/hr	Room
6	400°/hr	600°C	1 hr.	400°/hr	800°C	1 hr.	400°/hr	900°C	2 hrs.	400°/hr	Room
7	400°/hr	600°C	1 hr.	400°/hr	800°C	1 hr.	400°/hr	850°C	1 hr.	Step	Room

Where “Step” is defined as the fastest rate at which the furnace can heat or cool.

Production of Doped Samples

Powders were weighed according to the formula $Mg_{1.2-x}A_xB_2$, where A was Titanium, Niobium, or Vanadium, and x = 0.05, 0.1, 0.15, and 0.2. The powders were mixed and ground for approximately 15 minutes in a marble mortar and pestle. The doped pellets were prepared for heating in the same manner as the pure MgB pellets. Heat treatments 1 and 7 were used on the doped samples.

Results

The purity of MgB_2 was assessed using X-ray Diffraction. The purest sample showed virtually no MgB_4 or MgO, the two impurities plaguing MgB_2. Heat treatment 7 proved to be the best for formation of MgB_2. Heat treatment 1 was the second best, having the least amount of MgB_4 out of all other heat treatments, excluding 7. Heat treatment 7 applied to $Mg_{1.2}B_2$ resulted in the purest sample.

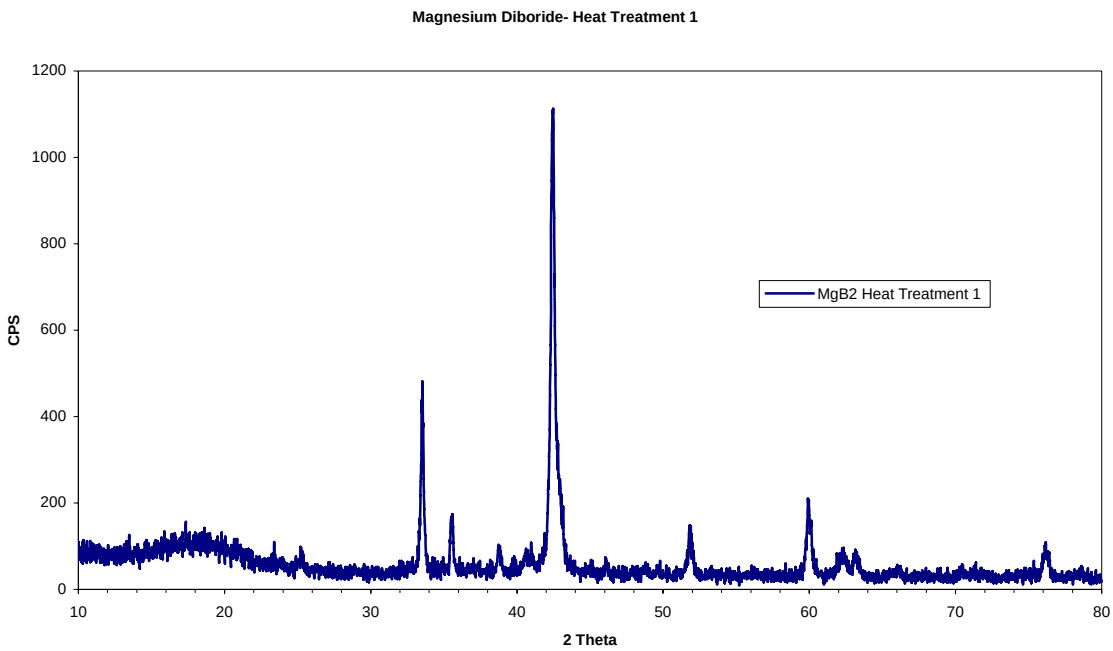

Figure 1. MgB_2 heat-treated to 900°C by treatment 1.

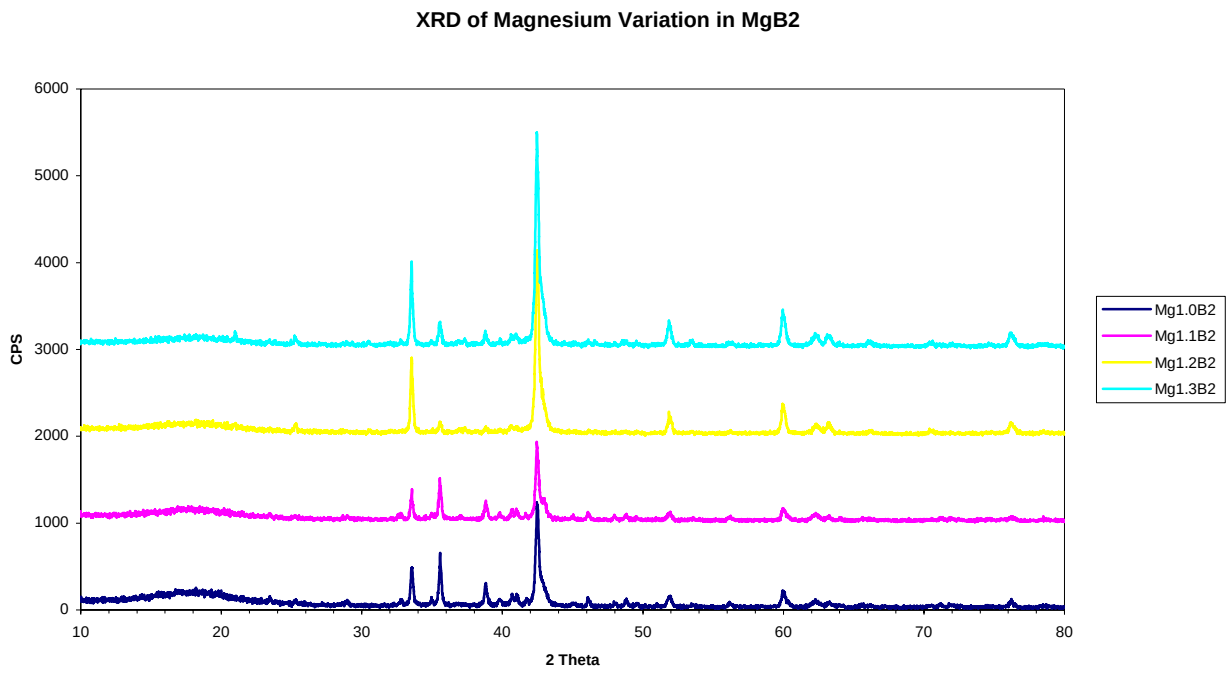

Fig. 2. $Mg_{1.2}B_2$ shows the purest MgB_2. Heat treatment 1 was used.

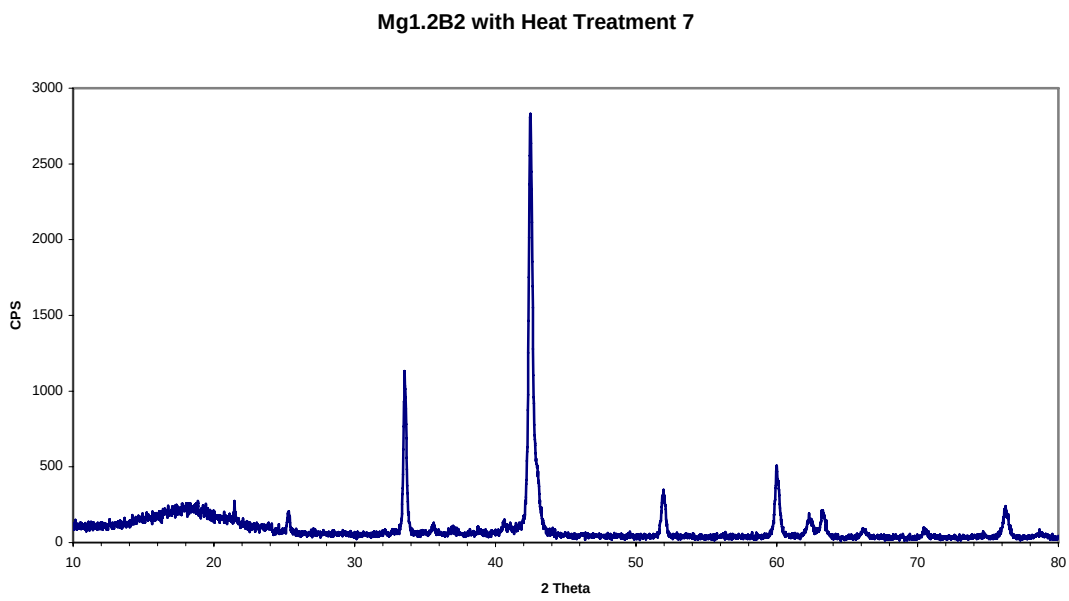

Figure 3. $Mg_{1.2}B_2$ heated using treatment 7. This is the purest sample.

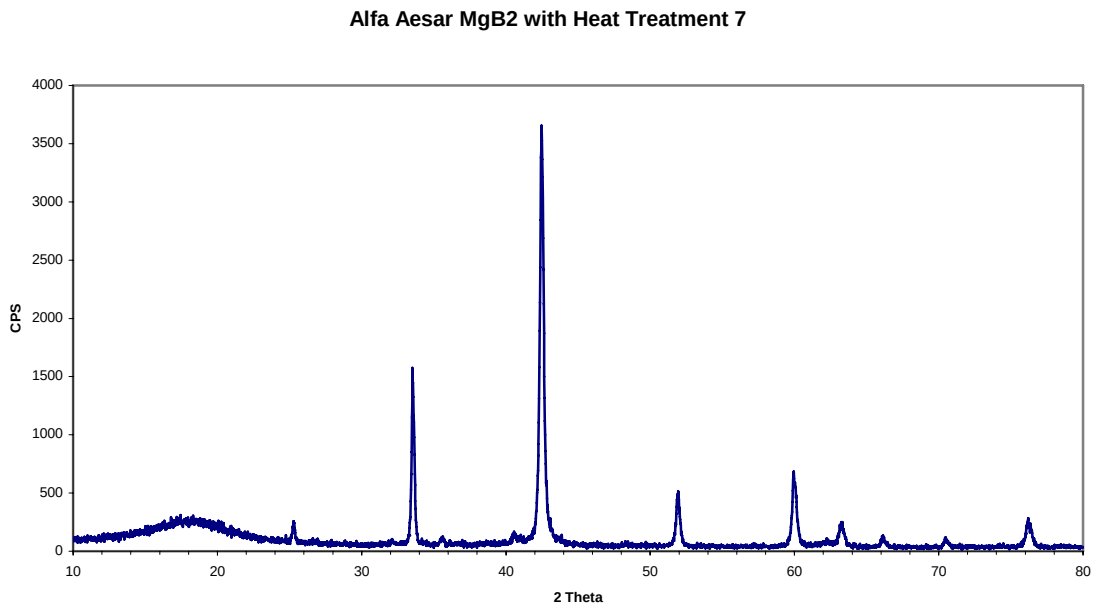

Figure 4. Alfa Aesar MgB_2 heat-treated using treatment 7.

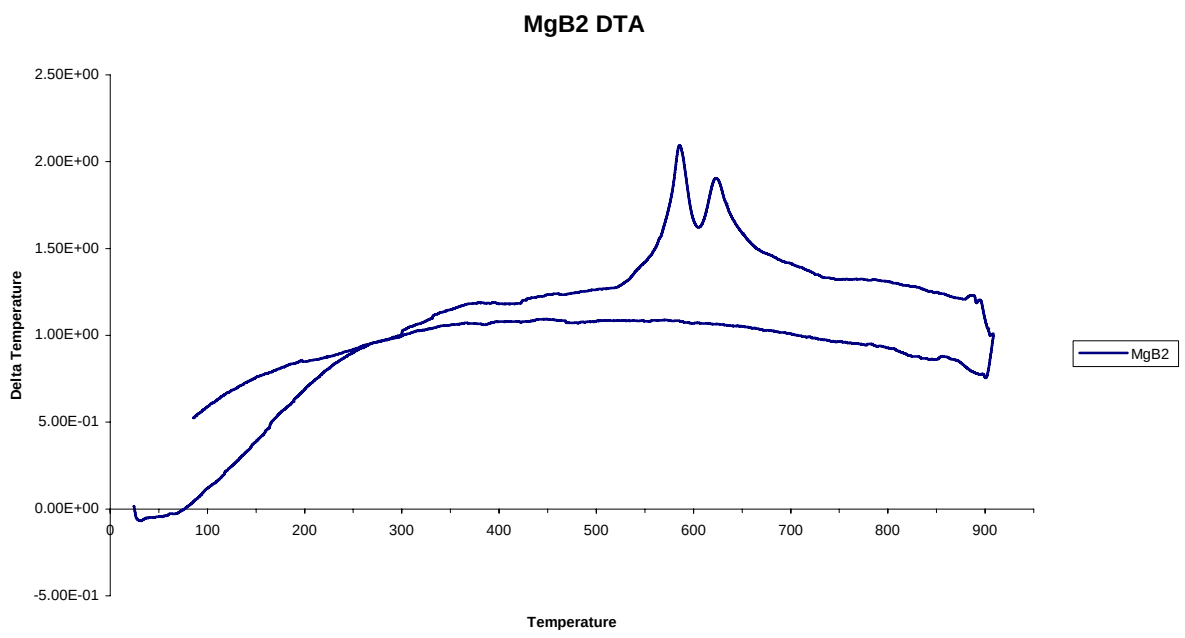

Figure 5. Differential thermal analysis of an MgB_2 sample. The test was taken from 100°C to 900°C and inversely from 900°C to 100°C.

The doped samples were subjected to heat treatments 1 and 7. In some doped samples, very small peaks of TiB_2 and VB_2 were observed in their XRD patterns. Others showed no evidence of compounds. $Mg_{1.15}V_{0.5}B_2$, $Mg_{1.1}Ti_{0.1}B_2$, and $Mg_{1.1}V_{0.1}B_2$ were the most promising samples for SQUID analysis due to small TiB_2 and VB_2 peaks found their XRD patterns. $Mg_{1.1}Nb_{0.1}B_2$ was not tested since there was a high concentration of MgB_4 and no sign of any Niobium compounds.

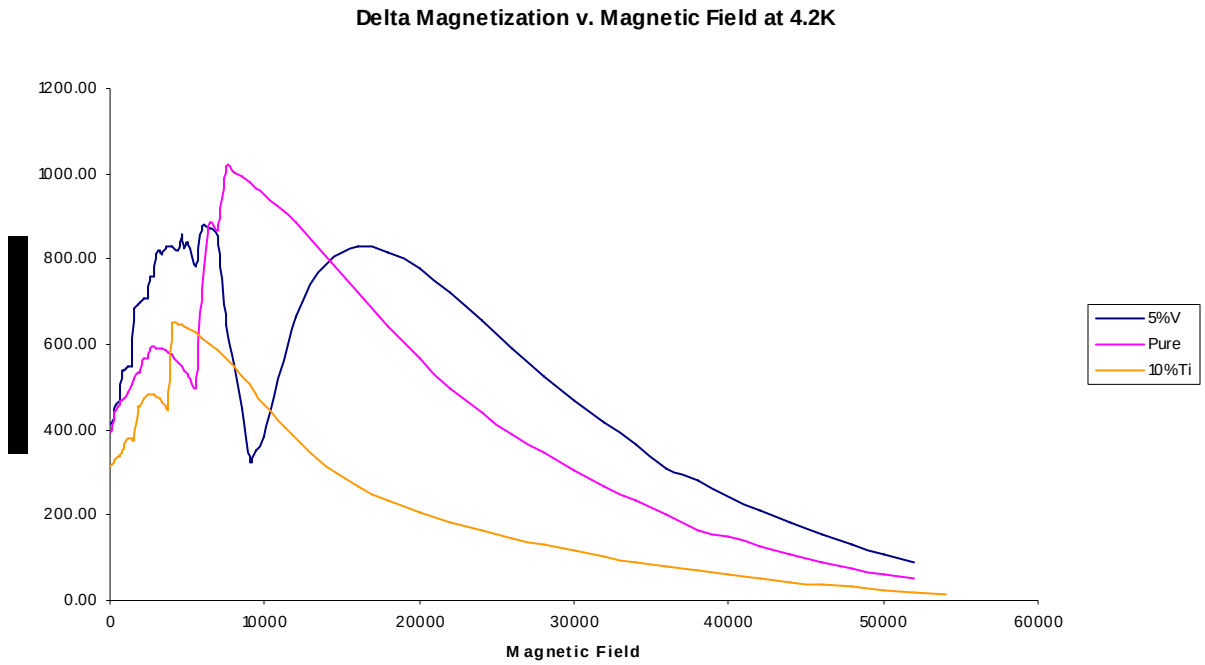

Figure 6. Delta Magnetic Moment verses Magnetic Field for 5% Vanadium, Pure $Mg_{1.2}B_2$, and 10% Titanium.

Discussion

In addressing the formation of MgB_4 in the MgB_2 samples, it was found that Magnesium evaporation and high temperatures were to blame. Magnesium evaporation proved to be problematic since this evaporation leads to the formation of MgB_4. Missing Magnesium causes a decrease in the Mg:B ratio, making the MgB_4 state energetically favorable. Encasing the samples in a non-reactive metal (Nickel foil) helped control evaporation and curbed the amounts of MgB_4 in the material.

To stop evaporation further, the ratio of Magnesium to Boron was increased by 10% three times. A 20% molar increase in Magnesium proved to be the best in curbing evaporation and erasing MgB_4 as determined by the XRD patterns.

DTA showed that around 900°C another phase transformation occurs in Magnesium and Boron. The heat treatment experiments along with their corresponding XRD patterns support that this transformation near 900°C can be attributed to the formation of MgB_4. The energy change is small in the DTA, but it is argued that since the sample was encased during testing, Magnesium

evaporation was minimal and the driving force for MgB_4 was not great. The furnace conditions are such that Magnesium evaporation is greater and therefore avoiding 900°C is beneficial. Lowering the last dwell temperature to 850°C improved the samples greatly.

XRD patterns were compared between an $Mg_{1.2}B_2$ pellet made from Magnesium and Boron powders and a pellet made from commercial MgB_2 powder. Both pellets were heat-treated using treatment 7 in the same furnace. The MgB_2 made from separate powders proved to as good as the commercially produced MgB_2.

The SQUID results for MgB_2 were consistent with those found in other papers. Unfortunately the results for the Titanium doped MgB_2 could not be reproduced. Most of the DTA results for doped samples showed several transitions after 900°C, which might account for the formation of compounds in the grain boundaries of MgB_2. Due to time constraints, further heat treatments beyond 900°C were not possible, and that may have been one cause for unimproved sample properties in the Titanium samples. Despite unimproved properties found in Titanium doped samples, the 5% Vanadium sample showed promising I_c measurements from its hysteresis found in Figure 6. The mechanism for flux pinning is not known for the Vanadium sample. Pinning through grain boundaries or perhaps through impurity defects are two possibilities. Further study is needed to make any conclusions.

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