Doping of Bulk MgB_2 Superconductor

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Abstract

Production of pure MgB_2 from magnesium and boron powders was accomplished by perfecting heat-treatment techniques and increasing the ratio of magnesium:boron to 1.2:2. The dopants titanium, vanadium, and niobium were then introduced as $Mg_{1.2-X}B_2M_X$ where X={0, 0.05, 0.10, 0.15, 0.20} and M is the dopant. Limited analysis of the doped samples showed promising results for vanadium, with X=0.05 vanadium doping showing a wider hysteresis curve than pure MgB_2.

Introduction

The recently discovered Type II superconductor Magnesium Diboride is positioned to replace Type I superconductors currently used in many applications. Its low cost and complexity coupled with its high Tc of roughly 40K suggest MgB_2 as an effective alternative to NbTi and Nb_3Sn. In order to rival Nb_3Sn, the Hc and Jc of MgB_2 must first be improved. Y. Zhao and colleagues demonstrated that doping the compound with titanium in the ratio $Mg_{0.9}B_2Ti_{0.1}$ resulted in a Jc of $2x10^6$ A/cm^2 at T=5K [1], a significant increase in critical current attributable to flux pinning. This success led us to examine the effects of doping with titanium, vanadium, and niobium.

Methods

Production of Pure MgB_2

Alfa Aesar 99.8% pure magnesium and 99.99% pure boron powders were combined in a 1:2 molar ratio and mixed using a mortar and pestle for 15 minutes. The resulting powder was then pressed into four 1 gram pellets under 2 metric tons of pressure. These pellets were placed in nickel foil boxes and heated in flowing argon using one of five heat treatments shown in Figure 1, each varying slightly from that reported by Y. Zhao. The resulting samples were examined for MgB_2 purity using an X-ray diffraction machine. By placing the pellets in unreactive nickel foil boxes and heating four pellets at a time we hoped to minimize magnesium loss due to evaporation, thus reducing MgB_4 formation. Treatments 1 and 6 showed lowest MgB_4 formation and thus were used in the doping portion of the experiment.

The X-ray diffraction analysis of the heat-treated pellets showed unacceptable MgB_4 presence in even the best sample. In order to further counteract magnesium evaporation the magnesium:boron molar ratio was increased. Four 1 gram pellets of 1:2 1.1:2 1.2:2 and 1.3:2 magnesium:boron powder mixtures were sintered using heat-treatment 1. MgB_4 presence decreased noticeably as magnesium was added, with a minimum at the ratio 1.2:2 as Figure 2 illustrates.

Doping

Alfa Aesar 99.99% pure titanium, 99.99% pure niobium, and 99.5% pure vanadium were chosen as dopants. Titanium was used in an effort to reproduce the improvements reported by Y. Zhao, while vanadium and niobium were selected for their ability to form compounds with boron. The goal of doping was to form a small percentage of compounds where boron bonded to the dopant, thus introducing flaws into the MgB_2 lattice at grain boundaries. These flaws would

hopefully enhance the pinning of magnetic flux lines in the material, producing greater Jc and Hc.

Magnesium and boron powders were mixed with titanium, vanadium, and niobium using mortar and pestle for 15 minutes, producing $Mg_{1.2-X}B_2M_X$ where X={0, 0.05, 0.10, 0.15, 0.20} and M is the dopant. For each doping percentage heat treatments 1 and 6 were applied. Each furnace run consisted of four 1 gram pellets (1 pure, 1 titanium, 1 vanadium, 1 niobium) individually boxed in unreactive nickel foil and heated in flowing argon. This yielded a total of 32 pellets from 8 separate furnace runs. Each of these pellets was then crushed and analyzed using X-ray diffraction to determine the amount non-superconducting MgB_4 present. The most promising samples were then measured for critical temperature and magnetic hysteresis using a SQUID. Hysteresis measurements were made at 4.2K, 10K, 18K, and 30K.

Discussion

As X increased from 0 to 0.2 in the doping scheme, formation of MgB_4 increased as well probably due to lower amounts of magnesium forcing the formation of higher borides. X-ray diffraction patterns of the samples were examined to determine if the desired compounds of TiB_2, VB_2, or NbB_2 formed. Unfortunately, the theoretical limit for X-ray diffraction to detect a compound is 5% content in the sample, which was a higher percentage than our samples could exhibit. Alternately, we hoped to identify promising samples by lower formation of MgB_4. If the dopants formed compounds with boron, this would remove boron from the sample thus lowering the probability of formation for higher boron compounds such as MgB_4. As Figure 3 illustrates, both vanadium and titanium doped samples contained only slightly more MgB_4 than pure samples, while niobium doped samples exhibited significant MgB_4 formation. Time constraints allowed SQUID analysis of only a few samples, thus the vanadium and titanium doped samples with best X-ray diffraction patterns were selected for comparison with pure MgB_2.

Magnetization measurements showed no change in Tc values for the samples, as all tested samples had a Tc of 38-39K. However, magnetic hysteresis measurements demonstrated a significant difference in hysteresis curve widths between the doped samples and pure MgB_2. Figure 4 shows the width of the hysteresis curves for pure MgB_2 prepared with heat treatment 1, plotted as delta M versus applied magnetic field. Figure 5 shows the hysteresis curve widths for 2 of the doped samples plotted against that of pure MgB_2. While $Mg_{1.1}B_2Ti_{0.1}$ exhibited smaller curve width than pure MgB_2, $Mg_{1.15}B_2V_{0.05}$ showed larger curve width. This is possibly due to improved flux pinning caused by impurities introduced in the lattice structure. Microstructural SEM analysis of the samples is needed to confirm this hypothesis. The wider hysteresis curves exhibited by the vanadium doped sample indicate improved current carrying abilities of the material, a hypothesis that needs to be tested by performing physical critical current measurements.

Conclusion

Production of pure MgB_2 was accomplished by applying the previously described heat treatment techniques to $Mg_{1.2}B_2$. The dopants titanium, vanadium, and niobium were then introduced as $Mg_{1.2-X}B_2M_X$ where X={0, 0.05, 0.10, 0.15, 0.20} and M is the dopant. Limited analysis of the doped samples showed promising results for vanadium, with X=0.05 vanadium doping showing a wider hysteresis curve than pure MgB_2, indicating higher Jc due to improved

flux pinning. Further SQUID analysis and critical current measurements on the prepared samples is required to solidly prove gains for vanadium doping.

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Treatment	Rate 1	Plateau 1	Hold 1	Rate 2	Plateau 2	Hold 2	Rate 3	Plateau 3	Hold 3	Cool
1	400°C /hr	600°C	1hr	400°C /hr	800°C	1hr	400°C /hr	900°C	1hr	Step
2	400°C /hr	600°C	1hr	400°C /hr	800°C	1hr	400°C /hr	900°C	1hr	400°C /hr
3	Step	600°C	1hr	Step	800°C	1hr	Step	900°C	2hr	Step
4	Step	600°C	1hr	Step	800°C	1hr	Step	900°C	2hr	400°C /hr
5	400°C /hr	600°C	1hr	400°C /hr	800°C	1hr	400°C /hr	900°C	2hr	400°C /hr
6	400°C /hr	600°C	1hr	400°C /hr	800°C	1hr	400°C /hr	850°C	1hr	Step

Figure 1. Heat Treatment Table.

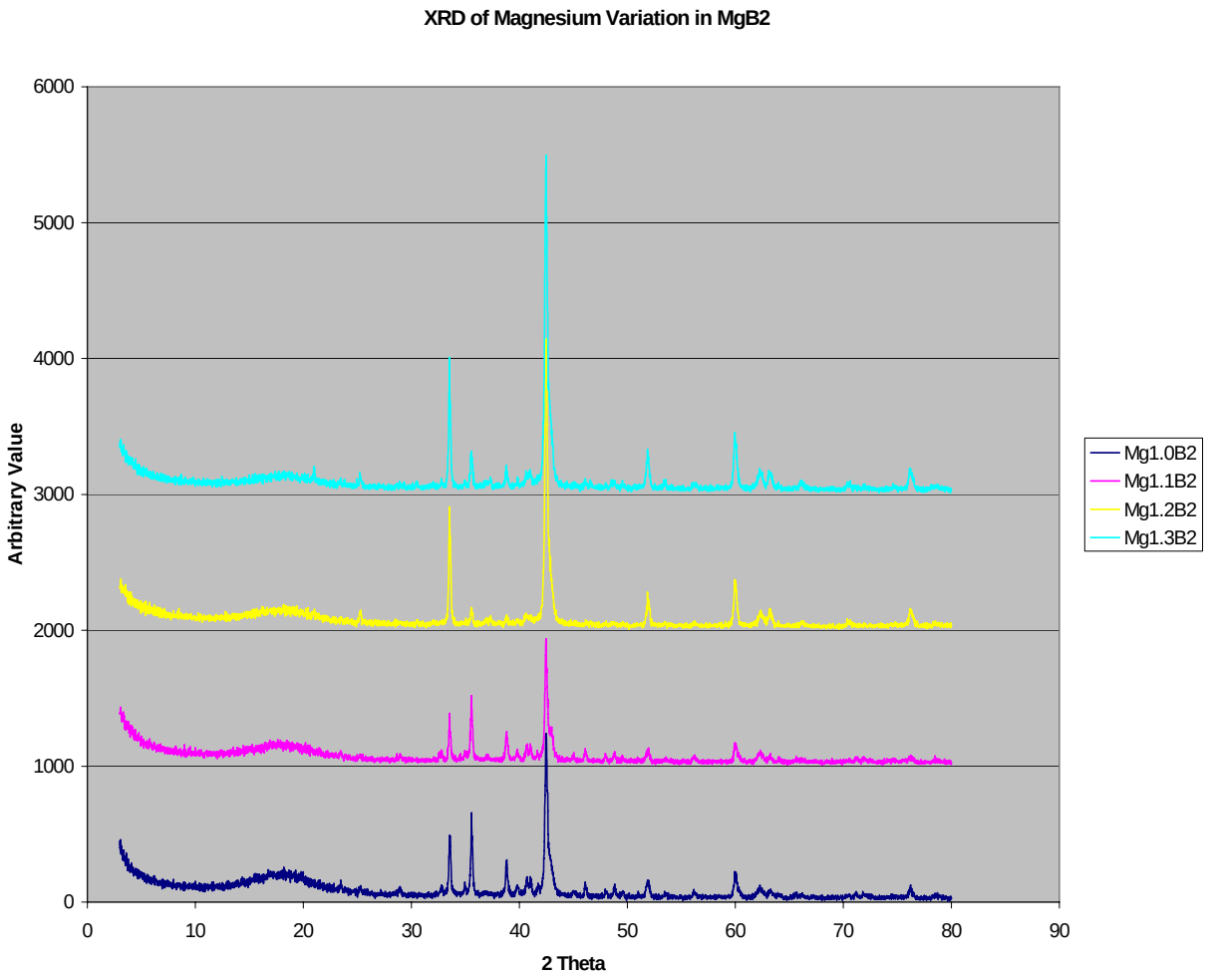

Figure 2. Magnesium Variation Results.

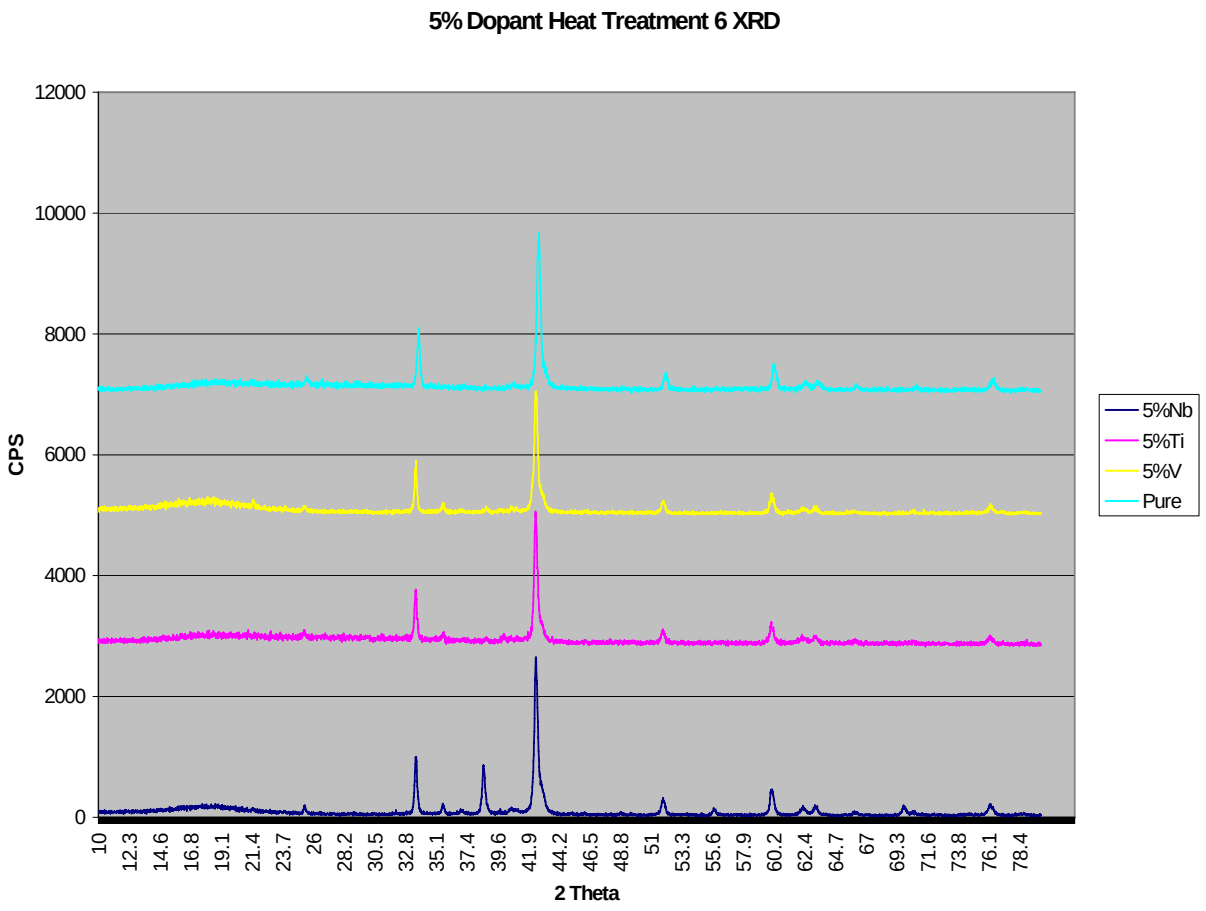

Figure 3. Example XRD Pattern of Doped Samples.

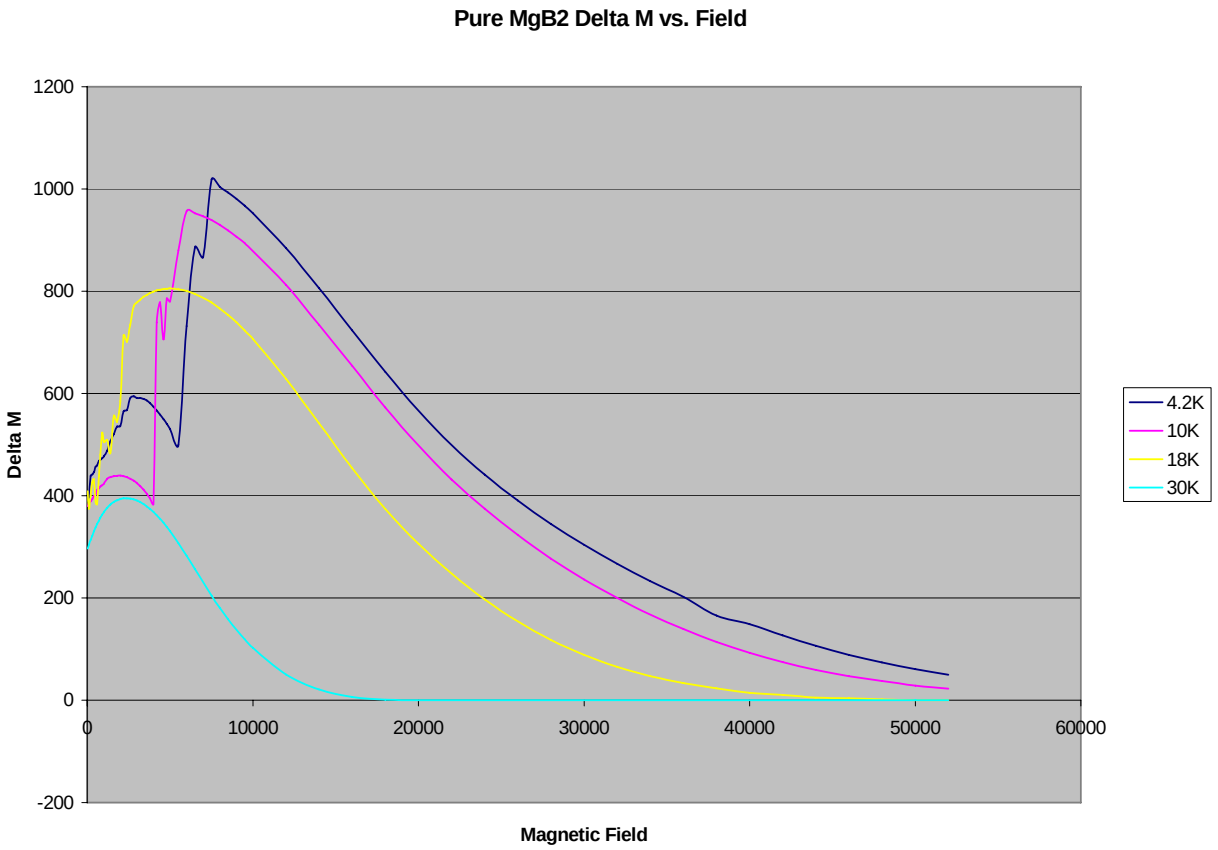

Figure 4. Hysteresis Curve Width for Pure MgB_2.

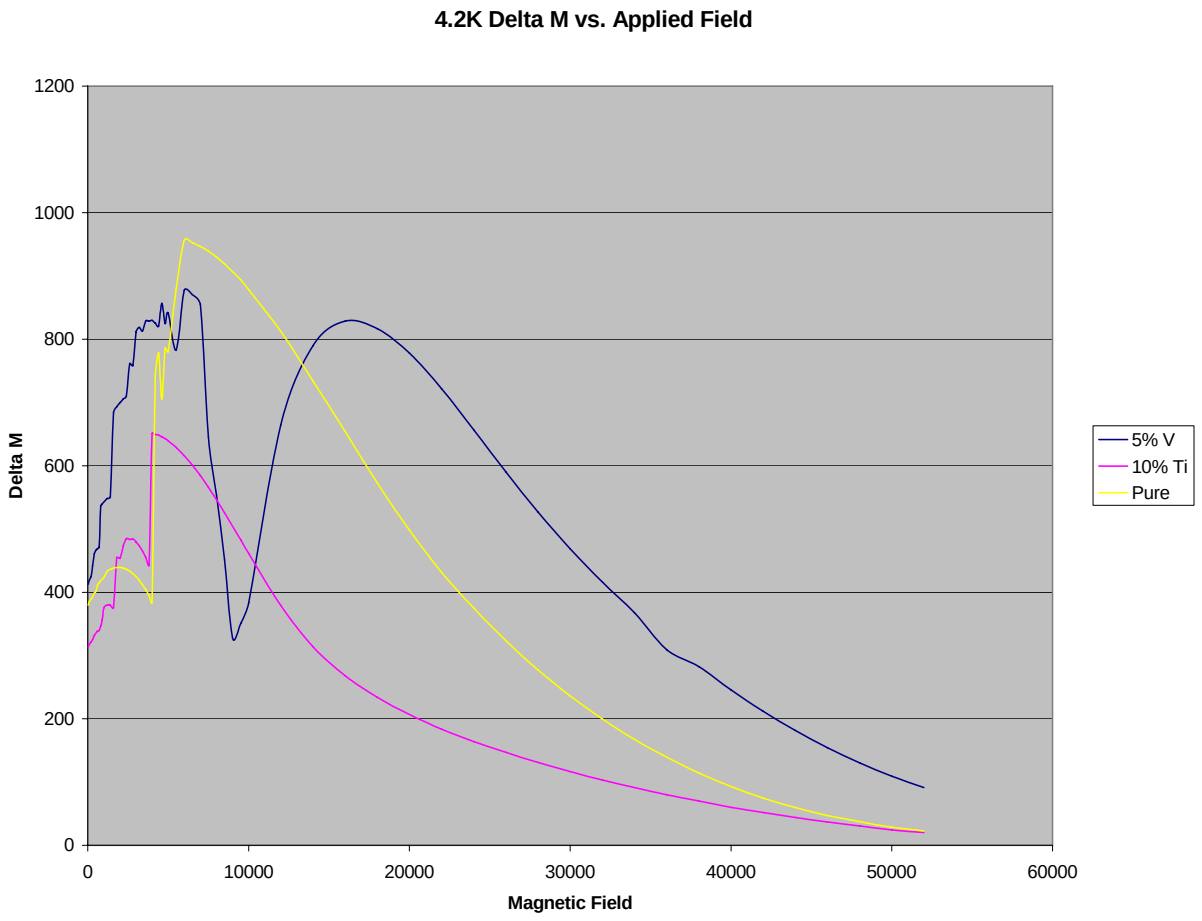

Figure 5. Hysteresis Curve Widths for Doped Samples.