Synthesis of Bulk Superconducting Magnesium Diboride

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ABSTRACT

Bulk polycrystalline superconducting magnesium diboride, MgB_2, samples were successfully prepared via a one-step sintering program at 750°C, in pure Argon with a pressure of 1atm. Both electrical resistivity and magnetic susceptibility measurements confirmed the superconductivity of the material at 39K, with a transition width of 5K. The polycrystalline nature, granular morphology, and composition of the sintered bulk material were confirmed using X-ray diffractometry (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray analysis (EDX).

Key words: magnesium diboride, synthesis, superconductivity

INTRODUCTION

The recent discovery of superconductivity in the intermetallic, binary compound magnesium diboride, MgB_2, with a superconducting transition temperature of 39K, (Nagamatsu et al., 2001) stimulated numerous investigations on the synthesis and characterization of this compound. MgB_2 shares many features with both 'conventional' superconductors and high-T_C cuprates, thus offering real progress in understanding superconductivity (Hirsch, 2001). Unlike the cuprates, MgB_2 has lower anisotropy, larger coherence lengths, and transparency of the grain boundaries to current flow. These make MgB_2 a promising candidate for higher operating temperature and higher speed devices (Buzea & Yamashita, 2001). Moreover, its simple crystal structure and metallic nature prove easier hurdles for the development of commercial applications (Rogado et al., 2001) than what is presented by the high-temperature cuprates.

Current progress on the synthesis of bulk superconducting samples of this material are both complex and involve the use of exotic materials. In most works, powders of Mg and B are mixed, then wrapped in iron (Dou et al., 2001), or tantalum foils (Larbalestier et al., 2001; Rogado et al., 2001), sealed in quartz ampoules (Zhao et al., 2001; Larbalestier et al., 2001), and then sintered at relatively high temperatures and pressures, ≈800-1000°C at ≥150MPa, (Indrakanti et al., 2001; Frederick et al., 2001) in ambient Ar/H_2 (Larbalestier et al., 2001) or Mg vapor atmospheres (Zhu et al., 2001). These preparations are multi-step processes. A single-step process in bulk synthesis is necessary for the successful growth of thin films of this compound. This may be the reason for the relatively low transition temperatures of ~24K-37K (Patnaik et al., 2001) reported for grown MgB_2 films so far. Transition temperatures reported for bulk MgB_2 are in the range of ~38.2K-39K (Dou et al., 2001; Larbalestier et al., 2001; Indrakanti et al., 2001; Frederick et al., 2001).

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This paper discusses the efforts by the Condensed Matter Physics Laboratory to prepare superconducting MgB_2. Results indicate that a one-step sintering process at a relatively low temperature of 750°C in an Ar atmosphere is promising for the synthesis of good, high quality bulk superconducting samples of MgB_2.

METHODOLOGY

Solid state reaction method

Initial attempts involved the solid state reaction of $MgCO_3$ and H_3BO_3. Stoichiometric amounts of these precursors were weighed and mixed, and then calcined at 500°C for 24 hours. Sequential sintering was performed on the calcined material at 900, 950, 980, and 1000°C for periods of 24 hours until a visible reaction of the precursors was observed.

Compaction and sintering in Ar

Commercial MgB_2 powder (Alfa Aesar, 99.9% pure) was utilized as starting material. Two samples weighing 4 grams each were compacted into pellets under 10 tons for 15 minutes. Electrical characterization was difficult because the pellets were granular and porous. These pellets were then sintered at 750°C and 780°C for 5 hours, respectively, in a pure Ar atmosphere of 1 atm pressure. The sintered pellets were then characterized via resistivity and AC magnetic susceptibility measurements. X-ray diffraction was used to identify the resulting phases in the sintered pellet while scanning electron microscopy was used to investigate its microstructure. Composition of the sintered sample was also determined using energy dispersive x-ray analysis.

RESULTS AND DISCUSSION

Solid state reaction

The initial attempts via solid state reaction of carbonates were unsuccessful. The calcined material was white in color and remained white despite the sequential sintering at high temperatures. Note that commercial MgB_2 powder is black in color. Also, the sintered product became noticeably harder at each sintering step. It was apparent that the proposed reaction did not take place. This may be due to the high volatility of Mg atoms at high temperatures (Shields et al., 2001). The volatility of Mg likely results in the formation of MgO (whitish in appearance) and/or other derivatives of Mg_xB_y. Also note that these sintering steps were done in air. Sintering in an ambient atmosphere without O_2 was thus concluded to be necessary in any synthesis of bulk samples of MgB_2.

Compaction and sintering in Ar

The sintered MgB_2 pellets were black in color with some grayish parts and were less granular and porous than the ones not yet sintered. Fig. 1 shows the measured resistivity plots of the two sintered MgB_2 pellets. A sharper transition was observed for the pellet sintered at 750°C (750C5H), compared to the incomplete transition for the pellet sintered at 780°C (780C5H). Also, pellet 750C5H has a higher transition temperature, T_C = 39.4K compared to the T_C = 31.5K of pellet 780C5H. The transition width for pellet 750C5H was 5K indicating good sample quality. On the other hand, the broad transition width of pellet 780C5H indicates that other phases are present in the bulk material. Therefore, pellet 750C5H is the better superconducting sample between the two.

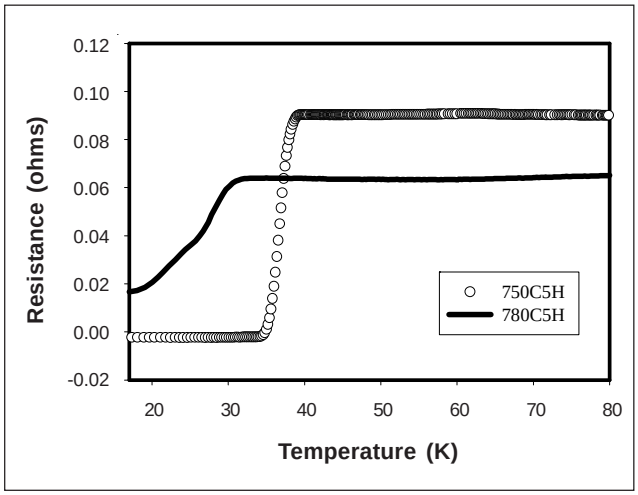

Fig. 1. Resistivity measurement plots of the sintered MgB_2 pellets. Open circles are for pellet 750C5H and closed circles are for pellet 780C5H.

Fig. 2 is a plot of the AC magnetic susceptibility of pellet 750C5H taken at a frequency of 800 Hz. The onset of the diamagnetic transition in the figure is at 39K, confirming the result of resistivity measurements. In addition, the diamagnetic transition is noticeably sharp, consistent with the results of resistivity measurements.

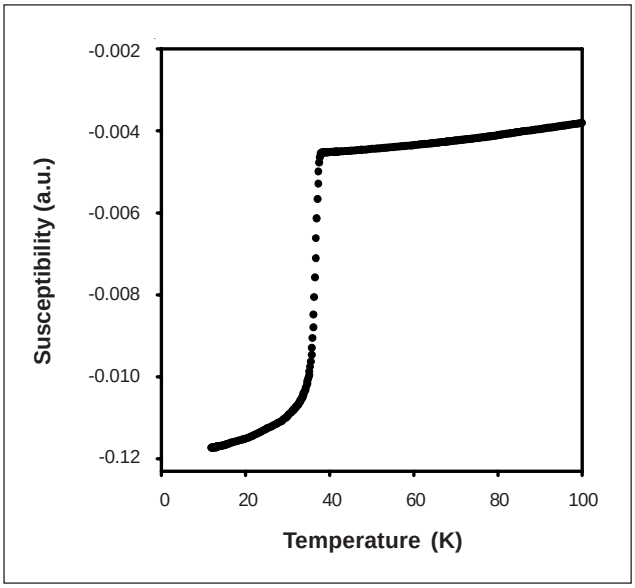

Fig. 2. AC magnetic susceptibility measurement plot of sintered MgB_2 (750C5H) at 800Hz. Diamagnetic transition starts at 39K.

The X-ray diffraction scan of pellet 750C5H is shown in Fig. 3. In the figure, the XRD pattern of the pellet is compared to the starting powder. From the figure, no significant difference between the sintered sample and the starting powder was observed. This implies that the sintered pellet is stoichiometrically MgB_2.

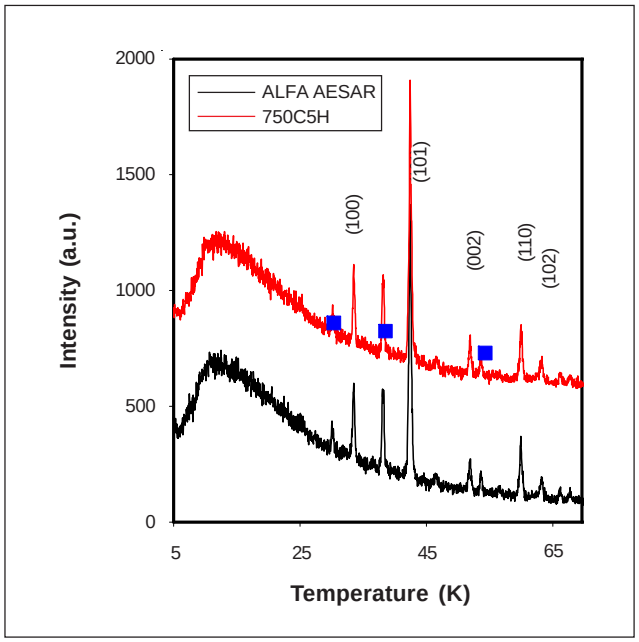

Fig. 3. X-ray diffractometry plot of sintered MgB_2 pellet 750C5H (light line) compared to that of the starting powder (dark line).

Lastly, the morphology of the sintered pellets is shown in the SEM micrographs depicted in Figs. 4 and 5. Fig. 4 shows the SEM image of sample 750C5H. The

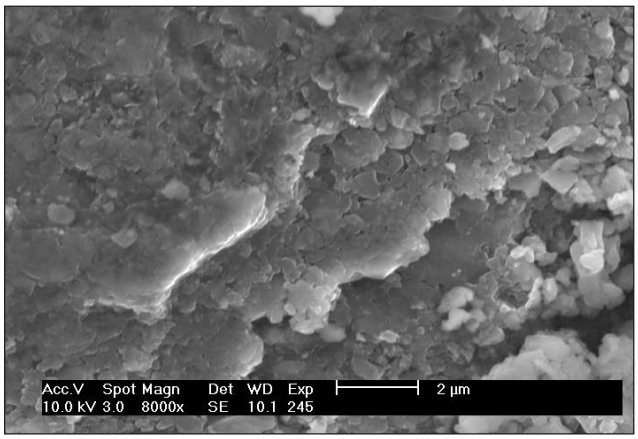

Fig. 4. Scanning electron micrograph of sintered MgB_2 pellet at 8000X (750C5H).

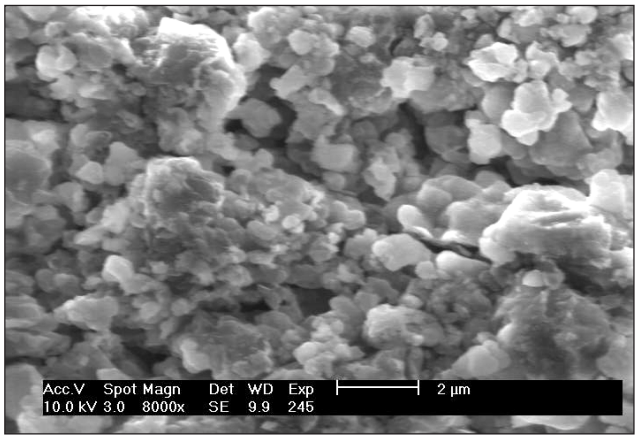

Fig. 5. Scanning electron micrograph of sintered MgB_2 pellet at 8000X (780C5H).

micrograph shows a relatively flat surface of compacted grains with small grain sizes. Note also the apparent black color of the grains (the color of MgB_2). Fig. 5, on the other hand, shows the SEM image of sample 780C5H. The micrograph this time shows a rougher surface with larger grains. Also, the apparent color of the grains is generally whiter or lighter in color than those shown in Fig. 4, which may be attributed to more MgO present in this sample. However, EDX analysis showed the presence of MgO on both samples. Thus, the apparent color in the SEM micrographs is not a reliable measure of MgO content of the samples. Therefore, the higher transition temperature of sample 750C5H is not due to the presence or absence of MgO in that particular sample. Instead, it is more likely that the smaller grain size observed in sample 750C5H plays a more crucial role in its superconductivity.

CONCLUSIONS

Bulk superconducting samples of magnesium diboride have been prepared via a single sintering step at 750°C in a pure Ar atmosphere. The sintered pellet exhibit a T_C of 39.4K, confirmed by both resistivity and AC magnetic susceptibility measurements. A sharp transition width, approximately 5K, indicates good sample quality of the sintered pellet, which was later confirmed by x-ray diffractometry and scanning electron microscopy.

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