Effect of sintering temperature under high pressure in the superconductivity for MgB$_2$

C. U. Jung, Min-Seok Park, W. N. Kang, Mun-Seog Kim, Kijoon H. P. Kim, S. Y. Lee, and Sung-Ik Lee

National Creative Research Initiative Center for Superconductivity
and Department of Physics, Pohang University of Science and Technology,
Pohang 790-784, Republic of Korea
(March 22, 2022)

We report the effect of the sintering temperature on the superconductivity of MgB$_2$ pellets prepared under a high pressure of 3 GPa. The superconducting properties of the non-heated MgB$_2$ in this high pressure were poor. However, as the sintering temperature increased, the superconducting properties were vastly enhanced, which was shown by the narrow transition width for the resistivity and the low-field magnetizations. This shows that heat treatment under high pressure is essential to improve superconducting properties. These changes were found to be closely related to changes in the surface morphology observed using scanning electron microscopy.

PACS number: 74.25.Fy, 74.60.-w, 74.70.Ad, 74.72.-h

The recent discovery of superconductivity at about 40 K in MgB$_2$ has resulted in a surge of interest. Conventional BCS superconductivity has been proposed for this compound, and a shift in the $T_c$ due to the boron isotope has been reported with an isotope critical exponent of $\alpha_B \sim 0.26$. The type of carrier has been predicted to be positive with boron planes acting like the CuO planes in cuprate high-temperature superconductors.

We demonstrated a hole-type carrier for MgB$_2$ by using Hall measurements. Note that other transition metal borides, which are not superconducting, have been shown to have negative Hall coefficients.

Previously MgB$_2$ was synthesized from a stoichiometric mixture of Mg and B in a sealed Ta tube which was placed in a quartz ampoule at 950°C. However, these samples were found to be porous and mechanically weak. Some have reported the synthesis of dense pellets sintered under high pressures of several GPa, which makes it easy to study the transport properties. The physical properties for samples made at different pressures have been different from each other, yet so far, the effect of the synthesis conditions on the superconductivity has not been studied.

Now the binary intermetallic compound MgB$_2$ has become a strong candidate for superconductivity applications because of its metallic nature and its simple structure compared to oxide superconductors. Moreover, the compound is expected to be less anisotropic than layered high-temperature superconductors. However, the growth of a thin film has not yet been reported, the high melting temperature of boron being one of the major reasons. A proper target for synthesizing a thin film has not yet been fabricated. The most promising candidate is pulsed laser ablation technique, but large dense target is not yet available.

For large-scale device applications, as well as for small-scale electronic device applications, the relation between the synthesis conditions and the superconducting properties should be well established. Previously, we reported the transport properties of hard and dense MgB$_2$ sintered at 950°C under 3 GPa. We found a clear difference in the resistivity as a function of the temperature and the magnetic field between our sample prepared at high pressure and other bulk samples not prepared at high pressure. The metallic nature of our sample could be inferred from its shiny surface. This sample was strong enough to prepare an optically clean and flat surface for a reflectivity measurement after polishing.

In this paper we report the change in the resistivity near $T_c$, the low-field magnetization, and the surface morphology of MgB$_2$ with the sintering temperature at 3 GPa. As the sintering temperature of the MgB$_2$ pellet was increased from 500 to 950°C, the superconducting transition width for a 10 to 90% drop, $\Delta T_c$, decreased systematically while the onset temperature, $T_{on}$, was nearly the same. Scanning electron microscope images showed that these behaviors were accompanied by changes in the grain size and their connectivity.

A 12-mm cubic multi-anvil-type press was used for the high-pressure sintering. The starting material was a commercially available powder of MgB$_2$. The pressed pellet was put into a Au capsule in a high-pressure cell and pressurized up to 3 GPa. While the pressure was maintained, the heating was increased linearly; then, maintained at constant temperature for 2 hours. The samples were then quenched to room temperature. The S(500), S(700), S(800), and S(950) in this paper were pellets sintered at 500, 700, 800, and 950°C, respectively. The pellets, weighing about 130 mg, were about 4.5 mm in diameter and 3.3 mm in height. For samples sintered at temperatures higher than 950°C, the gold started to melt and to adhere strongly to the MgB$_2$.

A dc SQUID magnetometer (Quantum Design, MPMSX) and a field-emission scanning electron microscope (SEM) were used to investigate the low-field magnetization and the surface morphology. For the resistivity measurement, we cut the samples by using a diamond saw and then polished them into rectangular solid shapes with dimensions of about $1 \times 1 \times 4.5$ mm$^3$. The resistivity curve, $R(T)$, was measured by using a standard 4-probe
The resistivity values were normalized to 1.0 at 40 K, to observe the change in the superconducting transition width with the sintering temperature. The solid circles denoted by 20°C are for the pellet which was pressurized without subsequent heating for 3 GPa. The solid, dashed, dotted, and dash-dotted lines are for the pellet sintered at 950, 800, 700, and 500°C, respectively.

Figure 2 shows the normalized resistivity of the sintered pellets near \( T_c \). The resistivity values were normalized to \( R(40 \text{ K}) \), just above \( T_c \), for comparison. The solid circles represent the resistivity for the S(20) which was pressurized at 3 GPa without subsequent heating for a conducting current path. The solid, dashed, dotted, and dash-dotted lines are for S(950), S(800), S(700), and S(500), respectively.

As the sintering temperatures was increased from 500 to 800 °C, the \( \Delta T_c \) decreased systematically, but the \( T_{co} \) changed little. Also, the \( \Delta T_c \) of S(800) and S(950) were nearly the same, which indicates that the optimum sintering temperature region is wide under high pressure. The absolute value of the resistivity at 40 K of S(950) was nearly the same as that of S(800), but was about two times smaller than that of S(500).

Figure 2 shows the normalized magnetic susceptibility, \( 4\pi\chi(T) \), from the measured low-field magnetization of MgB₂. The solid circles are for the starting powder itself. The solid, dashed, dotted, and dash-dotted lines are for S(950), S(800), S(700), and S(500), respectively. The lines for S(950) and S(800) nearly overlay each other. The pronounced hump around 30 K shown for S(500) was due to a weak-link. This weak-link feature was also visible in the resistivity data in Fig. 1. As the sintering temperature was increased above about 700°C, the weak-line feature disappeared. These support that, in high pressure, originally-separated grains begin to develop a weak-link forms below 500°C, and gradually a strong-link. This trend will be shown in the following paragraphs. The decrease in superconducting transition width is more evident in the \( \chi_{ZF}(T) \) measurement than in the resistivity measurement. The field-cooling signal was found to mirror the \( \chi_{ZF}(T) \); namely the pinning seems to be enhanced as the sintering temperature is increased. For samples sintered above 800°C, the field-cooling signal was less than 0.5 percent of the zero-field-cooling signal.

Figure 3 shows SEM images of S(20), S(500), and S(950) with a magnification of 5,000. The scale bars are 1 µm in length. The image in Fig. 3 (a) is for S(20). Here, we can clearly see separated grains and voids. The grain size is less than about 0.5 µm. In Fig. 3 (b), some parts of the grains for S(500) adhered to each other while other parts of the grains remain isolated. In Fig. 3 (c), the S(950) pellet has grains that are very well connected with each other. We cannot even distinguish one grain from another over a wide area. Energy dispersive spectroscopy using SEM showed that gold used to wrap around the pellet smeared into the pellet by a depth of about 300 µm for S(950). This feature was very helpful for attaching electric pads and could be another small advantage of this material for electrical applications.

We observed well-interconnected changes in the transport and the magnetic properties, near \( T_c \), which were accompanied by the microscopic changes in the observed surface morphology of MgB₂. The strong connection between the grains with increasing sintering temperature seems to explain the change in the resistivity and the low-field magnetization.

We are thankful for the SEM work to Mr. D. S. Kim at the Department of Material Science and Engineering. Discussion with Dong-Wook Kim on the film growth is also acknowledged. This work is supported by the Ministry of Science and Technology of Korea through the...
The scale bars are 1 \( \mu m \) in length. The sintering temperatures were (a) 20\(^{\circ}\)C, (b) 500\(^{\circ}\)C, and (c) 950\(^{\circ}\)C. The sample without actual heating, S(20), shows well-separated grains with spacious voids. As the sintering temperature is increased, the connectivity of each grain increases and the porosity decreases rapidly.

* Electronic address: jungking@postech.ac.kr

1 J. Akimitsu, Symposium on Transition Metal Oxides, Sendai, January 10, 2001. J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, and J. Akimitsu. Submitted to Nature.

2 S. L. Bud’ko, G. Lapertot, C. Petrovic, C. E. Cunningham, N. Anderson, and P. C. Canfield. cond-mat/0101463 (2001), Phys. Rev. Lett. (in press).

3 J. Kortus, I. I. Mazin, K. D. Belashchenko, V. P. Antropov, and L. L. Boyer. cond-mat/0101440 (2001).

4 J. E. Hirsch. cond-mat/0102113 (2001).

5 W. N. Kang, C. U. Jung, Kijoon H. P. Kim, Min-Seok Park, S. Y. Lee, Hyeong-Jin Kim, Eun-Mi Choi, Kyung Hee Kim, Mun-Seog Kim, and Sung-Ik Lee, cond-mat/ (2001), submitted to Phys. Rev. Lett.

6 H. J. Juretschke and R. Steinitz, J. Phys. Chem. Solids 4, 118 (1958).

7 R. W. Johnson and A. H. Daane, J. Chem. Phys. 38, 425 (1963).

8 D. K. Finnemore, J. E. Ostenson, S. L. Bud’ko, G. Lapertot, and P. C. Canfield. cond-mat/0102114 (2001).

9 Paul Mackenie, private communication.

10 C. U. Jung, Min-Seok Park, W. N. Kang, Mun-Seog Kim, S. Y. Lee, and Sung-Ik Lee, cond-mat/ (2001).

11 Y. Takano, H. Takeya, H. Fujii, H. Kumakura, T. Hatano, K. Togano, H. Kito, and H. Ihara, cond-mat/0102167 (2001).

12 D. C. Larbalestier, M. O. Rikel, L. D. Cooley, A. A. Polyanskii, J. Y. Jiang, S. Patnaik, X. Y. Cai, D. M. Feldmann, A. Gurevich, A. A. Squitieri, M. T. Naus, C. B. Eom, E. E. Hellstrom, R. J. Cava, K. A. Regan, N. Rogado, M. A. Hayward, T. He, J. S. Slusky, P. Khalifah, K. Inumaru, and M. Haas, cond-mat/0102210 (2001).

13 D. B. Chrisey and G. K. Hubler, Pulsed Laser Deposition of Thin Films (John Wiley & Sons, 1994).

14 C. U. Jung, J. Y. Kim, Mun-Seog Kim, Min-Seok Park, Heon-Jung Kim, Yushu Yao, S. Y. Lee, and Sung-Ik Lee, submitted to Physica C.

15 Alfa Aesar, A Johnson Matthey Company, Stock # 88149: magnesium boride, 98% (assay) MgB\(_2\) (possible impurities are not specified).