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# Improvement of critical current density in MgB$_2$ superconductors by Zr doping at ambient pressure

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We present the superconducting properties and phase compositions of $Mg_{1-x}Zr_xB_2$ bulk samples fabricated by a solid-state reaction at ambient pressure. It is found that a small amount of Zr atoms may be introduced into the lattice of MgB$_2$, while the majority of them forms ZrB$_2$ phase. The $Mg_{0.9}Zr_{0.1}B_2$ sample shows the highest $J_C$ of $2.1\times10^6$ A/cm$^2$ in 0.56 T at 5 K and $1.83\times10^6$ A/cm$^2$ in self-field at 20 K, higher irreversibility field and larger upper critical field in MgB$_2$ bulk samples. The combination of good grain connection, the reduction of grain size and small ZrB$_2$ particles in the sample may be responsible for the significant enhancement of $J_C$ in Zr-doped samples. This technique has a great potential to prepare high performance MgB$_2$ bulk samples and wires on an industrial scale. © *2001 American Institute of Physics.*
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The recent discovery of superconductivity at 39 K in binary intermetallic compound MgB$_2$ has attracted much more interest.[1] The critical temperature $T_C$ value of MgB$_2$ is much higher than the previous record $T_C$ of 23 K for the A15 compound Nb$_3$Ge. Unlike high-$T_C$ superconductors, MgB$_2$ has no weak link at the grain boundaries.[2] It is found that MgB$_2$ is a typical type-II superconductor, very similar to Nb$_3$Sn except for the extremely high $T_C$.[3,4] Unfortunately, the MgB$_2$ bulk samples prepared under ambient pressure have a low $J_C$ (the highest $J_C$ is around $2\times10^5$ A/cm$^2$ at 10 K in zero field) due to the bad connection between grains and poor flux pinning.[5] To date, high quality MgB$_2$ bulk samples have been fabricated by using high pressure.[6,7] The typical $J_C$ value of these samples could reach $2\times10^4$ A/cm$^2$ at 20 K in 1 T.[6] It is also reported that dense MgB$_2$ bulks with $J_C$ of $1.4\times10^6$ A/cm$^2$ at zero temperature can be obtained by using hot isostatic pressing.[8] Although these techniques, including high pressure sintering and proton irradiation, can be used to improve the flux pinning,[9] they suffer from the technical problems and are not suitable for the fabrication of MgB$_2$ wires and tapes. On the other hand, the chemical doping is found to be easily controlled, nondestructive and highly efficient in improving microstructure and flux pinning in high-$T_C$ superconductors.[10] Very recently, it was observed that the partial substitution of Zn or Cu for Mg in MgB$_2$ led to a

reduction of $T_C$.[11] In addition, contrary to an article describing a deleterious effect of Ti doping,[12] a previous study shows a suitable amount of Ti doping will increase $J_C$ in MgB$_2$.[13]

In this letter, magnetization, x-ray diffraction results and microstructure features in Zr-doped MgB$_2$ bulk samples are reported. The results indicate that the Zr doping can significantly enhance the flux pinning. The $J_C$ value of $2.1\times10^6$ A/cm$^2$ in 0.56 T at 5 K has been obtained in $Mg_{0.9}Zr_{0.1}B_2$, which is much higher than the best result reported so far in MgB$_2$ bulks.

The samples with nominal compositions of $Mg_{1-x}Zr_xB_2$ ($x=0$, 0.05, 0.1, and 0.2) were fabricated by the solid-state reaction method at ambient pressure by using the high purity powders of Mg (99%), Zr (99%), and B (99%). The precursor powders were fully mixed and were cold pressed into small cylindrical pellets. Then, the pellets were put on a Ta plate and heat treated at the temperature region of 600 °C to 900 °C for 3 h in flowing argon without high pressure. Finally, the pellets were followed by a furnace cooling to room temperature. Magnetization was measured by a superconducting quantum interference device magnetometer (Quantum Design, MPMSR2) at different temperatures in the magnetic field up to 7 T. $J_C$ values were deduced from the magnetization curves using the Bean critical model.[14] The phase composition analysis of all samples was carried out by an ac 10000 x-ray diffractometer with a Cu $K\alpha$ irradiation.

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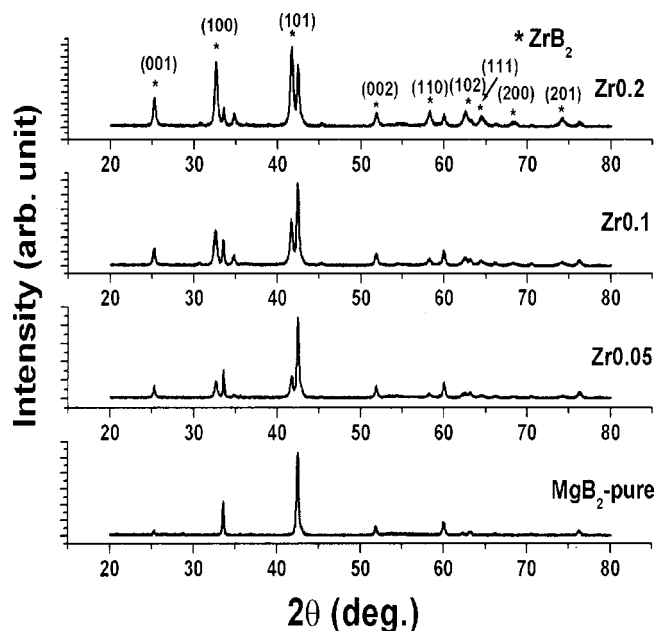
FIG. 1. X-ray diffraction patterns for all samples. $ZrB_2$ phase is found in Zr-doped specimens.

All the samples for this study have the same dimensions of $0.7 \times 0.9 \times 1.4 \, \text{mm}^3$.

X-ray diffraction patterns for all samples are shown in Fig. 1. The results show that the $MgB_2$ crystalline grains in the sample are not textured. It can be observed that the $ZrB_2$ phase is formed besides the $MgB_2$ phase and the amount of $ZrB_2$ increases with an increase of Zr content in Zr-doped samples. The molar percentage of $ZrB_2$ in the samples increases from 3.63% in $Mg_{0.95}Zr_{0.05}B_2$ to 14% in $Mg_{0.8}Zr_{0.2}B_2$. Furthermore, the lattice parameters are calculated by the least-square fitting. The a axis increases with an increase of the doping level and the *c* axis remains almost unchanged, which indicates that a small amount of Zr atoms may be a substitute for Mg in the lattice of $MgB_2$. However, the lattice constants in the sample with $x = 0.2$ are the same as those in $Mg_{0.9}Zr_{0.1}B_2$, implying that the solubility limit is achieved in the sample with $x = 0.1$.

Figure 2 shows the temperature dependence of magnetization for all the samples at 20 Oe. It can be seen that critical

temperature changes with Zr doping and slightly decreases from 38.4 K in pure $MgB_2$ to 37.3 K in $Mg_{0.8}Zr_{0.2}B_2$. The slight variation of the $T_C$ in Zr-doped samples may be due to the partial substitution of Zr for Mg. The expansion of the a axis results in the reduction of $T_C$ in Zr-doped specimens, which gives evidence of the model of hole superconductivity in $MgB_2$.[15] In this model, it is predicted that the increase of the a axis will decrease the $T_C$. It is noted that the sample with $x = 0.1$ displays a superconducting transition at 37.3 K with a sharp transition width of 0.7 K, suggesting the phase homogeneity and good connection between grains. In addition, $Mg_{0.8}Zr_{0.2}B_2$ has the same $T_C$ as the sample with $x = 0.1$, but the transition width becomes slightly larger. This may be attributed to the solubility limit and more second phases existing in the sample. As shown in Fig. 3, the transitions in zero-field cooling (ZFC) and field-cooling (FC) processes for $Mg_{0.9}Zr_{0.1}B_2$ are dramatically separated, confirming the strong flux trapping in the sample with $x = 0.1$.

Figure 4 illustrates the $J_C$ value as a function of magnetic field at selected temperatures for the samples with $x = 0$, 0.05 and 0.1. All the Zr-doped samples have a higher $J_C$ than pure $MgB_2$. Within all temperatures and the whole field region up to 7 T, the $J_C$ value of the sample with $x = 0.1$ is the highest amount these samples. It can be seen from Fig. 4 that $J_C$ achieves $2.1 \times 10^6 \, \text{A/cm}^2$ in 0.56 T and



FIG. 3. Temperature dependence of magnetization in ZFC and FC conditions for $Mg_{0.9}Zr_{0.1}B_2$ at 20 Oe.
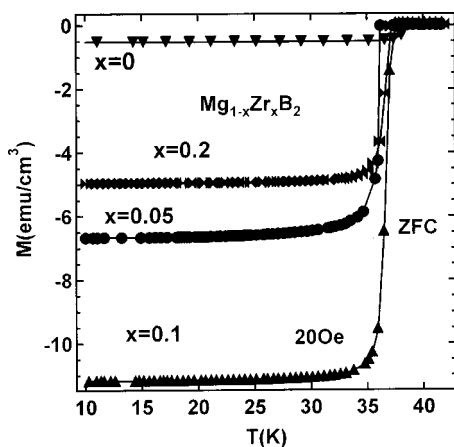


FIG. 2. Temperature dependent magnetization curves measured in ZFC condition at 20 Oe for all samples. The sample with $x = 0.1$ has the maximum diamagnetic signal.
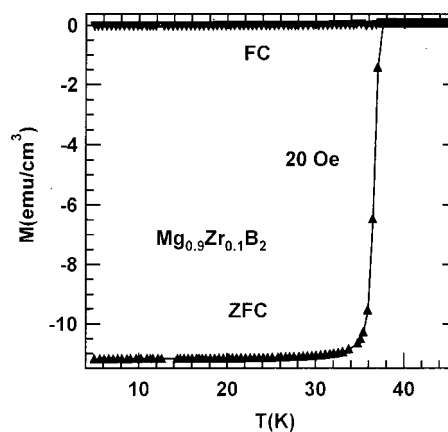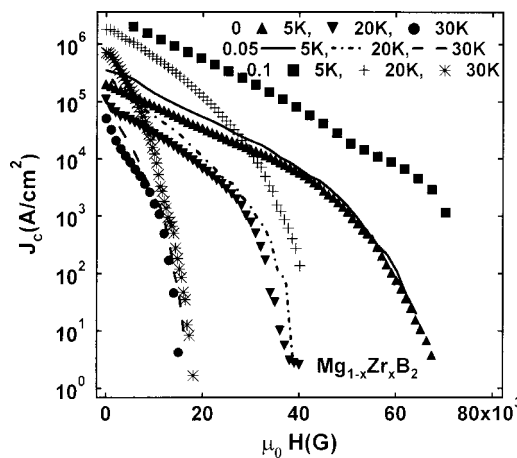


FIG. 4. $J_C$ versus magnetic field at 5, 20, and 30 K for the samples with $x = 0$, 0.05 and 0.1. Note that $J_C$ in $Mg_{0.9}Zr_{0.1}B_2$ is very high about 2.1 $\times 10^6 \, \text{A/cm}^2$ in 0.56 T at 5 K.

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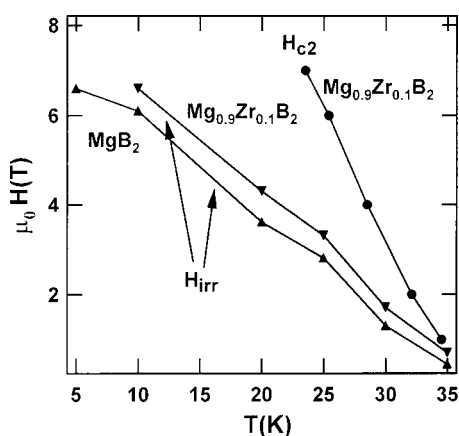


FIG. 5. Irreversibility fields as a function of temperature for pure $MgB_2$ and $Mg_{0.9}Zr_{0.1}B_2$ samples. The $H_{c2}$ data for the sample with $x=0.1$ is also shown.

$5.7 \times 10^5$ A/cm$^2$ in 2 T at 5 K for the $Mg_{0.9}Zr_{0.1}B_2$ sample. At 20 K, $J_C$ is as high as $1.83 \times 10^6$ A/cm$^2$ in self-field, $5.51 \times 10^5$ A/cm$^2$ in 1 T and $1.22 \times 10^5$ A/cm$^2$ in 2 T. Also, $J_C$ reaches $7.2 \times 10^5$ A/cm$^2$ in self-field and $1.2 \times 10^4$ A/cm$^2$ in 1 T even at 30 K. These $J_C$ values are much higher than the best data on the $MgB_2$ bulk samples including proton-irradiated fragments, hot isostatic pressed sample and $MgB_2$ specimen prepared under high pressure. The Zr doping in $MgB_2$ opens up an effective and easily controlled method to improve $J_C$. It should be noted that this technique is very suitable for the industrial scale fabrication of $MgB_2$ bulks and wires because the Zr-doped samples are prepared at ambient pressure.

Moreover, the temperature dependence of the irreversibility fields $H_{irr}$ for pure $MgB_2$ and $Mg_{0.9}Zr_{0.1}B_2$ samples is shown in Fig. 5. The Zr doping also results in an improvement of $H_{irr}$. At 20 K, $H_{irr}$ is increased from 3.6 T in pure $MgB_2$ to 4.3 T in $Mg_{0.9}Zr_{0.1}B_2$. The irreversibility field in the sample with $x=0.1$ is much higher than those in the dense $MgB_2$ samples due to high pressure sintering. In addition, the upper critical field $H_{c2}$ for $Mg_{0.9}Zr_{0.1}B_2$ is also given in Fig. 5. The slope of the $H_{c2}-T$ curve is $dH_{c2}/dT = -0.56$ T/K, which yields a higher upper critical field $H_{c2}(0)=20$ T in $MgB_2$ bulks.

The mechanism for the significant enhancement of critical current density may be related to the very strong pinning force and its high density in Zr-doped $MgB_2$. First, the connection between the grains is much improved in Zr-doped samples. As the doping content increases, the density and $J_C$ value increase. The density of the Zr-doped sample is even higher than that of the $MgB_2$ specimens prepared under high pressure. However, the best microstructure is achieved in $Mg_{0.9}Zr_{0.1}B_2$. Secondly, the grain boundary pinning is very strong in $MgB_2$ like $Nb_3Sn$. The flux pinning force density is found to be inversely proportional to the grain size in $Nb_3Sn$.[16] The grain size of $MgB_2$ is reduced in the samples with high doping level. The average grain size in $Mg_{0.95}Zr_{0.05}B_2$ is around 90 nm, almost the same as that in pure $MgB_2$. When Zr content is increased to $x=0.1$, the average grain size is decreased to 60 nm, which will greatly

enhance the flux pinning. The grain size in $Mg_{0.9}Zr_{0.1}B_2$ is much smaller than those around $0.4-8.0$ $\mu$m in the samples fabricated under high pressure.[17] Besides the reduction of the grain size, very small $ZrB_2$ particles are formed in the $MgB_2$ matrix, which has a contribution to flux pinning in Zr-doped samples. At the low doping level of $x=0.05$, the density is higher than pure $MgB_2$, but not as high as in $Mg_{0.9}Zr_{0.1}B_2$. Therefore, the $J_C$ value in this sample is larger than that in pure $MgB_2$, but much smaller than that in $Mg_{0.9}Zr_{0.1}B_2$. Although the sample with $x=0.2$ has higher density and smaller grain size (30 nm), $J_C$ is still lower than that of $Mg_{0.9}Zr_{0.1}B_2$. This is due to the decrease of the amount of $MgB_2$ phase and the increase of the $ZrB_2$ phase.

In summary, highly dense $MgB_2$ bulk samples can be prepared by Zr doping through solid-state reaction under ambient pressure. The Zr doping leads to the formation of $ZrB_2$ in the sample and a small substitution of Zr for Mg. By $x=0.1$ doping in $Mg_{1-x}Zr_xB_2$, $J_C$ can be significantly enhanced to $2.1 \times 10^6$ A/cm$^2$ in 0.56 T and $5.7 \times 10^5$ A/cm$^2$ in 2 T at 5 K. At 20 K, $J_C$ is as high as $1.83 \times 10^6$ A/cm$^2$ in self-field, $5.51 \times 10^5$ A/cm$^2$ in 1 T and $1.22 \times 10^5$ A/cm$^2$ in 2 T. Also, this sample has a higher irreversibility field and upper critical field. It can be believed that the excellent grain connection, the reduction of grain size and very small $ZrB_2$ particles contribute to the great enhancement of the flux pinning.

[1] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, and J. Akimitsu, Nature (London) **410**, 63 (2001).
[2] D. C. Larbarlestier, M. O. Rikel, L. D. Cooley, A. A. Polynaskil, J. Y. Jiang, S. Patniak, X. Y. Cai, D. M. Feldman, 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. Slisky, P. Khalifah, K. Inumara, and M. Haas, Nature (London) **410**, 186 (2001).
[3] M. S. Kim, C. U. Jung, M. S. Park, S. Y. Lee, H. P. Kim, W. N. Kang, and S. I. Lee, Phys. Rev. B **64**, 012511 (2001).
[4] D. K. Finnemore, J. E. Ostenson, S. L. Bud'ko, G. Lapertot, and P. C. Canfield, Phys. Rev. Lett. **86**, 2420 (2001).
[5] M. Kambara, N. H. Babu, E. S. Sadki, J. R. Cooper, H. Minami, D. A. Cardwell, A. M. Campbell, and I. H. Inoue, Supercond. Sci. Technol. **14**, L5 (2001).
[6] Y. Takano, H. Takeya, H. Fuji, H. Kumakura, T. Hatano, K. Togano, H. Kito, and H. Ihara, Appl. Phys. Lett. **78**, 2914 (2001).
[7] H. H. Wen, S. L. Li, Z. W. Zhao, Z. A. Ren, G. C. Che, H. P. Yang, Z. Y. Liu, and Z. X. Zhao, Chin. Phys. Lett. **18**, 816 (2001).
[8] N. A. Frederick, S. Li, M. B. Maple, V. F. Nesternko, and S. S. Indrakanti, cond-mat/0106518.
[9] Y. Bugoslavsky, G. K. Perkins, X. Qi, L. F. Cohen, and A. D. Caplin, Nature (London) **411**, 561 (2001).
[10] Y. Feng, J. G. Wen, N. Koshizuka, and L. Zhou, Appl. Phys. Lett. **70**, 2984 (1997).
[11] S. M. Kazakov, M. Angst, and J. Karinski, cond-mat/0103350.
[12] S. Jin, H. Mavoori, and R. B. Vandover, Nature (London) **411**, 563 (2001).
[13] Y. Zhao, Y. Feng, C. H. Cheng, L. Zhou, Y. Wu, T. Machi, T. Fudamoto, N. Koshizuka, and M. Murakami, Appl. Phys. Lett. **79**, 1154 (2001).
[14] C. P. Bean, Rev. Mod. Phys. **36**, 31 (1964).
[15] J. E. Hirsch, Phys. Lett. A **282**, 292 (2001).
[16] A. M. Campbell and J. E. Evets, Adv. Phys. **21**, 199 (1972).
[17] J. Q. Li, L. Li, Y. Q. Zhou, Z. A. Ren, G. C. Che, and Z. X. Zhao, Chin. Phys. Lett. **18**, 680 (2001).