Enhancement of critical current density of MgB$_2$ by doping Ho$_2$O$_3$

C. Cheng and Y. Zhao$^{a)}$

Key Laboratory of Advanced Technologies of Materials (Ministry of Education of China), Superconductivity R&D Center (SRDC), Southwest Jiaotong University, Sichuan 610031, China and School of Materials Science and Engineering, University of New South Wales, Sydney 2052, New South Wales, Australia

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Mg$_{1-x}$(Ho$_2$O$_3$)$_x$B$_2$ alloys were prepared by in situ solid state reaction to study the effect of magnetic Ho$_2$O$_3$ dopant on flux pinning behavior of MgB$_2$. Crystal structure, $T_c$, and $H_{c2}$ were not affected by Ho$_2$O$_3$ doping; however, $J_c$ and $H_{irr}$ were significantly enhanced. In 5 T field, the best sample ($x=3\%$) reached $J_c$ of $1.0 \times 10^5$, $2.0 \times 10^5$, and $1.2 \times 10^5$ A/cm$^2$ at 20, 10, and 5 K, respectively, much higher than those achieved by nonmagnetic impurity, such as Ti-, Zr-, and Y$_2$O$_3$-doped MgB$_2$. The observed magnetic Ho$_4$B$_4$ nanoparticles were attributed to be the source for the enhanced flux pinning effects. © 2006 American Institute of Physics. [DOI: 10.1063/1.2409368]

The discovery of superconductivity at 39 K in MgB$_2$ offers the possibility of wide engineering applications in a temperature range of 20–30 K, where the conventional superconductors cannot play any role because of low $T_c$. However, the commercialization of MgB$_2$-based superconducting technology depends critically on continuous improvement of the performance of MgB$_2$ material, especially the properties in high magnetic fields, including $H_{c2}$ and $J_c$. Among many methods, alloying with carbon seems to be the most effective to improve the pinning behavior of MgB$_2$. Magnetic impurities usually have a stronger interaction with magnetic flux line than nonmagnetic impurities and may exert a stronger force to trap the flux lines if they can be properly introduced into the superconducting matrix. Therefore, pinning sites with strong magnetic moment may play important role to further improve the pinning behavior of MgB$_2$.

In this work, Ho$_2$O$_3$ is used as a dopant for MgB$_2$ to introduce magnetic impurities. Significantly improvement of the irreversibility field ($H_{irr}$) as well as of $J_c$ in high fields is observed. Our results show that introducing magnetic impurities is an efficient way to improve the performance of MgB$_2$ in high magnetic fields.

Samples with a nominal composition of Mg$_{1-x}$(Ho$_2$O$_3$)$_x$B$_2$ ($x=0$, 0.1\%, 0.5\%, 1\%, 3\%, and 10\%) were prepared with solid state reaction method with starting powder materials of amorphous B (99.99\%), Mg (99.9\%), and Ho$_2$O$_3$ (99.999\%). The mean particle sizes of magnesium, boron, and Ho$_2$O$_3$ were about 1 $\mu$m, 200 nm, and 50 nm, respectively. After well ground in a glovebox for 1 h, the mixed powders were pressed into pellets of a diameter of 10 mm, sealed in iron tubes with excess Mg, sintered at 850 $^\circ$C for 2 h in flowing Ar, and finally quenched to room temperature.

Crystalline structure was studied by powder x-ray diffraction (XRD) using an X’Pert MRD diffractometer with Cu Ka radiation. Microstructure was analyzed with a scanning electron microscope (SEM) and a Philips field emission transmission electron microscope with energy-dispersive x-ray spectroscopy (EDX) analysis. Magnetization was measured using a 9 T physical property measurement system (Quantum Design). The typical sample size is $0.8 \times 0.8 \times 1.0$ mm$^3$. A magnetic $J_c$ was derived from the width of the magnetization loop $\Delta M$ based on the extended Bean model: $J_c=20\Delta M/[a(1-a/3b)]$. $H_{irr}$ was determined from emerging point of $M(T)$ curve measured in zero-field-cooling (ZFC) and field-cooling (FC) processes at various fields up to 7 T.

Figure 1 shows the XRD patterns for Mg$_{1-x}$(Ho$_2$O$_3$)$_x$B$_2$ samples. MgB$_2$ is found to be the main phase in all samples.

$^{a)}$Author to whom correspondence should be addressed; FAX: +86-28-87600184; electronic mail: yzhao@swjtu.edu.cn
although impurity phases of HoB$_4$ and MgO are also observed in doped ones. No Ho$_2$O$_3$ was detected, suggesting that the reaction of Mg and B with Ho$_2$O$_3$ is nearly complete. Within the limit of calculation error, the $a$ and $c$ lattice constants obtained from Rietveld refinements did not change with the doping level, indicating that Ho is not doped into the MgB$_2$ lattice. The observed phase structure of the samples can be explained with the equation below:

$$x\text{Ho}_2\text{O}_3 + (1-x)\text{Mg} + 2\text{B} \rightarrow 2x\text{HoB}_4 + (1-4x)\text{MgB}_2 + 3x\text{MgO},$$

which shows that in a complete reaction between stoichiometric Ho$_2$O$_3$, B, and Mg, only three phases of HoB$_4$, MgB$_2$, and MgO can be presented.

As shown by $M(T)$ curves in ZFC [see Fig. 2(a)], all of these samples exhibit a sharp superconducting transition and a large diamagnetic shielding signal, indicating a good quality and uniformity of superconducting properties. The superconducting transition temperature $T_c$ spans between 37.1 and 37.3 K, indicating that Ho$_2$O$_3$ almost does not suppress the superconductivity of MgB$_2$. This is consistent with the XRD analysis which shows that Ho is not doped into the MgB$_2$ lattice. Although the signal of superconducting shielding [represented by $M(T)$ in ZFC] is slightly suppressed in heavily doped samples, the temperature-dependent characteristics of the signal are similar for those of the samples of different doping levels. In contrast to this, the flux exclusion features [reflected by the $M(T)$ curves in FC] change significantly with doping level, as shown in Fig. 2(b). Compared to the ZFC diamagnetic signal, 7% of the magnetic flux is excluded from the sample during the normal-to-superconducting transition in FC for the undoped MgB$_2$, whereas only 0.59% of the magnetic flux is excluded for 3% Ho$_2$O$_3$-doped MgB$_2$, indicating a significant enhancement of the flux trapping capability in the Ho$_2$O$_3$-doped sample. In addition, the temperature-dependent characteristic of magnetization in FC is also changed with doping level.

The unique behavior shown in Fig. 2(b) may be related with the existence of HoB$_4$ which possesses a strong magnetic moment. Therefore, it is necessary to further examine the magnetic properties of the samples in both the normal and the superconducting states. As shown in Fig. 2(c), in the normal state ($T=40$ K), all the doped samples exhibit strong paramagnetism which is enhanced significantly with increasing doping level. At temperature below 40 K, this paramagnetism coexists with superconductivity, as shown by the typical hysteresis loops for 3% Ho$_2$O$_3$-doped MgB$_2$ sample [see Fig. 2(d)], in which a strong paramagnetic background is superposed to the superconducting hysteresis loops. The coexistence of the paramagnetism and superconductivity is also observed in all of the Ho$_2$O$_3$-doped MgB$_2$ samples studied in this work.

Figure 3(a) shows the $J_c(H)$ curves for Mg$_{1-x}$(Ho$_2$O$_3$)$_x$B$_2$ samples at 5, 10, and 20 K. In the low field region, the Ho$_2$O$_3$-doped samples do not exhibit a significant improvement on $J_c$ of MgB$_2$. However, at all temperatures studied in this work, the $J_c$ in high field has been increased by Ho$_2$O$_3$ doping. The increase of $J_c$ is getting more pronounced with increasing doping level as $x<3\%$, but it begins to debase at $x=10\%$, suggesting that an optimal doping level for the increase of $J_c$ is between 3% and 10%. In a field of 5 T, the best sample ($x=3\%$) reaches $J_c$ of $1.0 \times 10^5$ A/cm$^2$ at 20 K, $2.0 \times 10^4$ A/cm$^2$ at 10 K, and $1.2 \times 10^5$ A/cm$^2$ at 5 K. For a comparison, when further increasing the doping level to 10%, the $J_c$ values in 5 T decrease to $1.5 \times 10^5$ A/cm$^2$ at 20 K, $1.1 \times 10^4$ A/cm$^2$ at 10 K, and $1.0 \times 10^5$ A/cm$^2$ at 5 K.

Quite different from the doping effects of Ti, Zr, Y$_2$O$_3$, and Dy$_2$O$_3$,5–9 which mainly improve the $J_c$ of MgB$_2$ in the low field region, Ho$_2$O$_3$ doping does not improve the low field $J_c$ significantly, but significantly improves the $J_c$ in the high field region. As shown in Fig. 3(a), around 5 K, the $J_c$ values of Ti- and Dy$_2$O$_3$-doped MgB$_2$ are much higher than that of the Ho$_2$O$_3$-doped sample when the field is lower than 2 T; however, these $J_c$ values decrease rapidly with further increasing the field, reaching a $J_c$ value much lower than that of the Ho$_2$O$_3$-doped sample in fields higher than 4 T. For
example, at 5 K, both 10% Ti- and 3% Ho2O3-doped MgB2 have a Jc around 2.0 × 10^4 A/cm^2 in a field of 4 T, but the Jc for Ti-doped one drops to a value of 9.0 × 10^3 A/cm^2 at 6.5 T, whereas the Ho2O3-doped one keeps a Jc higher than 7.0 × 10^4 A/cm^2 in this field, about eight times higher. Further increasing the field to 9 T, the Ho2O3-doped sample still sustains a Jc as high as 3.0 × 10^4 A/cm^2. The improvement of Jc-H behavior of MgB2 by Ho2O3 doping is also comparable with that achieved by nanocarbon-doped MgB2 in magnetic fields lower than 9 T (Ref. 4) [see also Fig. 3(a)].

Figure 3(b) shows the results of Hc1(T) and Hc2(T) for the samples with doping levels of 0, 1.0%, and 3.0%. The irreversibility field is improved gradually with increasing doping level. However, it is worthy to note that the Hc2 is almost not changed. This is quite different from C-doped MgB2 in which the improvement of Hc2 is closely related with the enhancement of Hc1. The difference between doping carbon and doping Ho2O3 in MgB2 is that the former introduces the dopant into the MgB2 lattice, affecting the intrinsic properties such as Tc and Hc2 of MgB2, and consequently improving both Hc1 and Jc, whereas the latter does not modify the intrinsic superconducting properties of MgB2 and only provides impurity phase serving as pinning centers. For this reason, Ho2O3-doped MgB2 can sustain a high Jc from low to high magnetic fields, whereas C-doped MgB2 possesses a high Jc in higher field region. It is expected that a combination of these two doping effects may result in an enhancement of Jc over a full range from low to very high magnetic fields.

Microstructural analyses are also employed to further elucidate the mechanism for the doping effect of Ho2O3 on MgB2. As shown in Fig. 4, SEM micrograph shows that the samples are tightly packed MgB2 nanoparticle structure with an average particle size of 50–100 nm. As reported previously, this type of nanostructure in MgB2 provides a good grain connection as well as the grain boundary flux pinning, sustaining a high Jc in low and medium high field regions (<4 T) for MgB2. Further, TEM micrograph reveals that highly dispersed nanoparticles with a size of 5–10 nm are inserted in the MgB2 matrix. EDX analysis reveals that these nanoparticles contain mainly Ho and B. Combining with the XRD analyses it can be deduced that these nanoparticles are HoB4. This deduction is consistent with the facts that main impurity phases in Y2O3- and Dy2O3-doped MgB2 are YB4 and DyB4, respectively.

As reported previously by several groups,10,11 HoB4 has a very strong magnetic moment. With decreasing temperature to below 5 K, HoB4 may even transform from a paramagnetic to a magnetic-ordering state. Because there are no other Ho-contained impurity phases detected by XRD, HoB4 should take the responsibility for the observed coexistence of the paramagnetism and superconductivity. In addition, these magnetic nanoparticles may provide stronger attraction force to flux lines than nonmagnetic impurities, thus enhance the flux pinning effect. This can be the reason that magnetic HoB4 nanoparticles are more effective flux pinning centers than those played by nonmagnetic nanoparticles.

In summary, Mg2-x(2x)O3-B2 alloys have been prepared by in situ solid state reaction. It is observed that Ho2O3 doping in MgB2 does not modify the crystal structure, keeping Tc and Hc2 largely unchanged; however, Jc and Hc1 have been significantly enhanced. The enhancement of Jc in high magnetic fields by doping the magnetic HoB4 is much more pronounced than that by doping the nonmagnetic impurities, such as Ti, Zr, Y2O3, etc. The magnetic HoB4 particles with a size between 5 and 10 nm are believed to take the responsibility for the enhanced flux pinning effects as well as for the coexistence of paramagnetism and superconductivity in the samples.

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