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Improved Superconducting properties in the Mg^{11}B_2 low activation superconductor prepared by low-temperature sintering

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Mg^{11}B_2 has a great application prospect in the superconducting coils for fusion reactor as the “low activation superconductors”. The un-doped Mg^{11}B_2 and Cu-doped Mg^{11}B_2 bulks using ^{11}B as a boron precursor were fabricated by low-temperature sintering in present work. It was found that the prepared Mg^{11}B_2 low activation superconductors exhibit better J_c performance than all of other Mg^{11}B_2 samples reported in previous studies. As for Cu doped Mg^{11}B_2 , minor Cu addition can obviously improve the Mg^{11}B_2 grain crystallization and reduce the amount of MgO impurity. Hence, improved grain connectivity and higher J_c at low fields is obtained in Cu doped Mg^{11}B_2 samples. For un-doped samples, refined grains and more MgO impurity with proper size brought about more flux pinning centers, resulting in better J_c performance at high fields.

The observation of superconductivity in MgB_2 at 39 K in 2001¹ has attracted lots of attention. MgB_2 shows excellent properties such as simple crystal structure, large coherence length, relatively high critical current density, and transparency of the grain boundaries and relatively low cost material. Using kinds of approaches, MgB_2 ^{2–9} has been fabricated into bulks, single crystals, thin films, tapes and wires in various methods^{10,11}. Taken together, these properties and preparation techniques support MgB_2 to be a promising candidate for important large-scale and electronic device applications.

The radioactivity decay time of all kinds of superconducting wire¹² who had broad application prospect in the international thermonuclear experimental reactor (ITER) Tokamak superconducting coil showed that Nb-based superconductor wires who have been widely used nowadays had a very long induction of radioactive decay time, so Nb-based superconductor wires needed much longer time to cool down. The longer cooling time brought negative impact on the environment and treating processes. Furthermore, despite their relatively high J_c ^{13–15}, Nb-based superconductors suffer high operation costs due to the usage of liquid helium as coolant. In contrast, MgB_2 radioactivity decay time is very short and has higher running temperature, so it has a great application prospect in the fusion reactor as the “low activation superconductors”. In general, the natural elementary boron is composed of 20% ^{10}B and 80% ^{11}B . In the irradiation environment, the reaction $^{10}\text{B} + n \rightarrow ^7\text{Li} + \text{He}$ (gas) will occur due to the large thermal neutron capture cross section of ^{10}B . Hence, as part of superconductor, there is no guarantee for the long-term stability of the MgB_2 superconducting magnet. Isotope research shows that ^{11}B is much more stable than ^{10}B in neutron irradiation environment due to the smaller neutron capture cross section¹⁶ which can ensure the operation stability of MgB_2 superconductor magnet. Previous studies have been focused on the theoretical calculation of isotope boron effect on the MgB_2 ^{17,18}, but little on the experiment research. Only a few previous experimental studies put many emphases on the performance of the Mg^{11}B_2 superconducting wires^{19,20}, which performed obviously different from the traditional MgB_2 wire with natural B powder, and the critical current density exhibits much lower than the traditional MgB_2 with natural B powder²⁰.

On the other hand, one can know that the traditional MgB_2 samples using natural boron powder which fabricated at low temperature generally had higher critical current density at high fields than those prepared at high temperature due to inferior crystallinity^{21–23}. However, the reaction at low temperature generally took a very long

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time to form the complete MgB_2 because of the low diffusion rate of atom in the solid-state below the melting point of Mg^{24} . Y. Hishinuma *et al.* also reported that the successful synthesis of Mg^{11}B_2 samples with higher J_c performance needs to take as long as 200 h by heating at 500°C^{20} . From this view, it makes sense to rapidly fabricate Mg^{11}B_2 samples with improved J_c by heating at low temperature.

In previous studies, the influence of Cu addition on the sintering process and superconducting properties of MgB_2 samples with natural boron powder were systematically studied^{25,26} and it was found that minor Cu addition was proved to benefit to the formation of MgB_2 phase at low temperature, and thus MgB_2 bulks with excellent J_c performance can be rapidly fabricated at low temperature by Cu activated sintering^{26,27}. Inspired by this, herein the influence of Cu addition on the Mg^{11}B_2 bulks with isotope ^{11}B powder will be studied and Cu addition is expected to benefit to its low temperature sintering process as well as superconducting properties. Actually, the research about the influence mechanism of Cu addition on the Mg^{11}B_2 bulks is seldom carried out till now.

Based on these backgrounds, in present study, we focused on the synthesis of Mg^{11}B_2 with higher superconducting properties by heating at low temperature for short holding time. In this study pure ^{11}B was used as the raw material instead of natural B, with the purpose of solving the tokamak plasma problem in controllable thermonuclear fusion. Besides the un-doped samples, we also investigated the phase formation and superconducting properties in the Cu-doped Mg^{11}B_2 samples. Combined with the measurement of the T_c and critical current density, the effects of the element ^{11}B and Cu addition on the superconducting properties of MgB_2 are concluded.

Experimental

The samples of un-doped Mg^{11}B_2 and $\text{Mg}^{11}\text{B}_2 + 5\text{wt.}\%$ Cu were prepared by a solid-state sintering at low temperature. ^{11}B powders (Amorphous, about $5\ \mu\text{m}$ in size, from Pavezyum Kimya, Turkey), Mg powders (99.5% purity, $100\ \mu\text{m}$ in size), and Cu powders (99.7% purity, $3\ \mu\text{m}$ in size) were separately mixed in the ratio of Mg^{11}B_2 and $\text{Mg}^{11}\text{B}_2 + 5\text{wt.}\%$ Cu. Then, the mixed powders were pressed into cylindrical pellets ($\Phi 5 \times 1.5\ \text{mm}$). All the un-doped and Cu-doped pellets were sintered in differential thermal analysis (Mettler Toledo TGA/DSC1/) respectively at 600°C for 5 h, 10 h and 15 h under flowing high-purity Ar gas with a heating rate of $10^\circ\text{C}\ \text{min}^{-1}$ and then cooled down to room temperature with a cooling rate of $40^\circ\text{C}\ \text{min}^{-1}$. The phase composition of the sintered samples was examined by X-ray diffractometer (XRD, Rigaku D/max 2500) using Cu $K\alpha$ radiation, and the morphology of the samples was characterized by scanning electron microscope (SEM, S-4800, Hitachi). The superconducting properties were measured by superconducting quantum interference device (SQUID VSM, Quantum Design), after the samples were cut into a slab of size about $4 \times 2 \times 1\ \text{mm}^3$. The corresponding J_c values were calculated from the width of magnetization hysteresis loops based on the Bean model $J_c = 20\Delta M/[a(1 - a/3b)]^{28}$, where ΔM is the volume magnetization, and a and b are the sample dimensions.

Results and Discussion

Figure 1 presents the XRD patterns of the un-doped and Cu-doped Mg^{11}B_2 samples sintered at 600°C for 5 h, 10 h and 15 h respectively. In the un-doped samples (see Fig. 1a), one can see that MgB_2 is the main phase which is different from the traditional MgB_2 sample with natural boron powder sintered at the same condition. In previous studies^{25,27}, it was reported that no obvious MgB_2 peaks can be observed in the un-doped MgB_2 samples sintered below 650°C only if some additional methods are employed, such as chemical doping^{29,30}. Besides, the peaks of residual Mg phase in the un-doped samples decrease as the holding time prolongs, indicating that longer sintering time could facilitate the reaction between Mg and ^{11}B forming Mg^{11}B_2 at low temperature. On the other hand, the residual Mg peaks cannot be recognized in all the Cu-doped samples. This implies that Cu addition can significantly promote the formation of Mg^{11}B_2 phase, just as the case of MgB_2 samples with natural boron powder^{25,29}. Local Mg-Cu liquid resulting from the eutectic reaction between Cu and Mg at about 485°C can enhance Mg diffusion and thus accelerate the formation of MgB_2 phase^{25,26}. Furthermore, comparing with the un-doped ones, the Cu-doped samples contain less MgO impurity. The decrease of MgO impurity owes to the existence of local Mg-Cu liquid which could wrap the neighboring Mg particles and thus protect them from the oxidation³¹.

Based on the X-ray diffraction patterns of samples, the full width at half maximum (FWHM) was obtained and shown in Fig. 2. One can see that the FWHM of MgB_2 peaks in the Cu-doped samples are smaller than that of un-doped ones. This result demonstrates that the size of MgB_2 grains in the Cu-doped samples is larger than un-doped ones. In previous studies^{10,11,31}, it was reported that the minor Cu addition can promote the growth of grain and improve the crystallization degree.

The sintering density of samples is present in Table 1. The density of all sintered samples is similar and about half of the theoretical value ($2.62\ \text{g}/\text{cm}^3$), but higher than the other ones in previous studies using the similar preparation technique³². Generally, the chemical reaction between Mg and B forming MgB_2 results in about 30% volume reduction and porosity is known to be difficult to avoid during the sintering process³³. This is the main reason why the *in-situ* sintering density of Mg^{11}B_2 bulks is generally lower than their theoretical value. In addition, the inevitable evaporation and oxidation of Mg during sintering process also have a negative impact on the sintering density. Interestingly, the sintering density of Cu-doped Mg^{11}B_2 samples was a little higher than that of un-doped samples. It could be explained that more sintering densification can occur in Cu doped samples due to the existence of local liquid sintering environment resulting from Mg-Cu liquid at low temperature. Besides, since the MgCu_2 impurity as a result of Cu addition possesses relatively higher density than MgB_2 , finally it can contribute to the higher sintering density of Cu doped samples.

The temperature dependence of magnetization curves for the un-doped and Cu-doped Mg^{11}B_2 samples were shown in Fig. 3, and the corresponding results were listed in Table 1. The transition temperature (T_c) of Mg^{11}B_2 samples is about 36 K, which is generally lower than the normal MgB_2 due to the isotope effect of $^{11}\text{B}^{17,18}$. But the critical temperature of our Mg^{11}B_2 bulks is comparable to other Mg^{11}B_2 samples²⁰, indicating that isotope effect is the key factor lowering T_c , rather than other processing conditions. It is worth noting that the critical temperature of all our samples is above 35 K which still meets the actual needs of practical applications. Besides, the transition

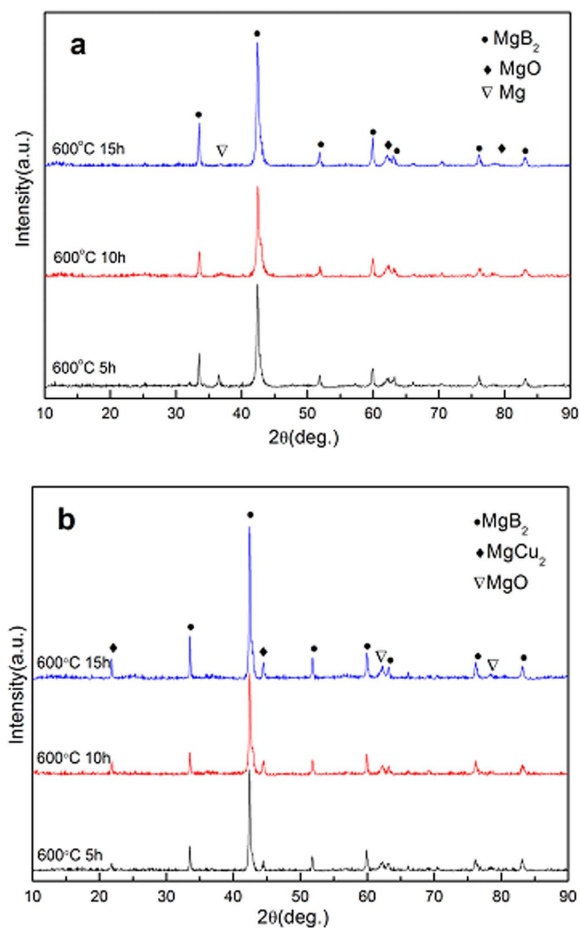


Figure 1. The XRD patterns of samples sintered at 600 °C for different heating time (a) un-doped MgB_2 and (b) Cu-doped MgB_2 samples.

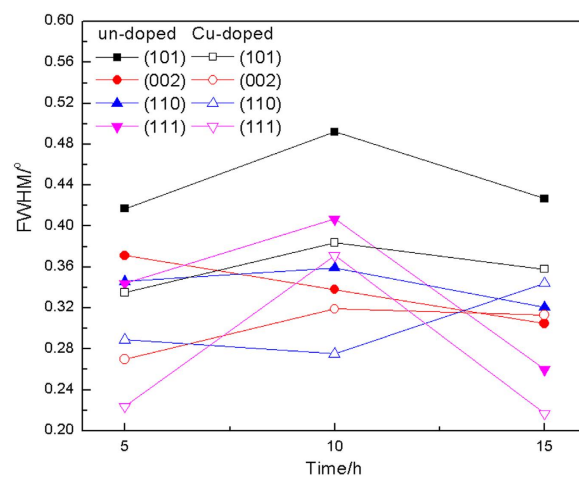


Figure 2. FWHM of the un-doped and Cu-doped samples prepared at 600 °C for 5 h, 10 h and 15 h. The corresponding planes of MgB_2 are (101), (002), (110) and (111), respectively.

width (ΔT), the interval between $T_{c, \text{onset}}$ and $T_{c, \text{end}}$ becomes broad as the sintering time prolongs. As all know, the high critical temperature and sharp transition width indicate that the samples are of high crystallinity and homogeneity. It is suggested that the increased sintering time can facilitate the reaction between Mg and B completely. With extend of holding time, indefinite quantity of impurities can be introduced, which may reduce the purity and homogeneity of samples.

Sample		ρ (g/cm ³)	T_c (K)	ΔT (K)	H_{irr} (T)	J_c at 3T, 20 K ($\times 10^3$ A·cm ⁻²)
Un-doped	5h	1.30	35.75	0.82	4.61	2.815
	10h	1.29	35.88	0.77	4.88	4.881
	15h	1.31	36.17	1.03	5.01	5.782
Cu-doped	5h	1.39	35.91	0.69	4.24	2.106
	10h	1.31	36.01	1.05	4.23	3.395
	15h	1.34	36.28	1.41	4.19	2.748

Table 1. The superconducting properties of the samples.

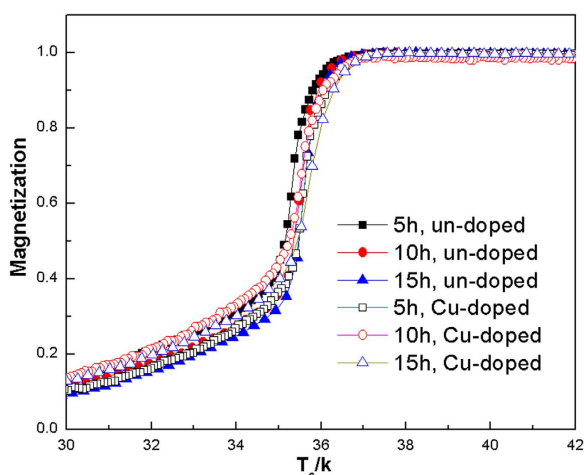


Figure 3. Temperature dependences of ZFC magnetization for the sintered samples.

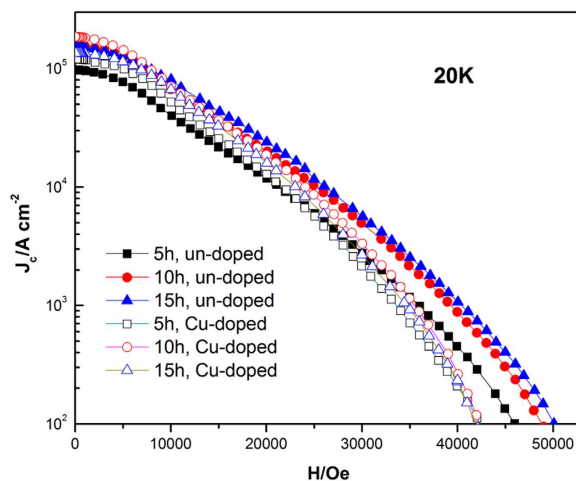


Figure 4. The measured J_c - H characteristics of the sintered samples at 20 K.

The critical current density (J_c) and irreversibility field (H_{irr}) of samples are illustrated in Fig. 4 and Table 1. The samples with Cu addition showed relatively lower J_c than the un-doped samples at high field, whereas higher J_c at low-field. Generally speaking, critical current density in MgB₂ is decided by both grain connectivity and flux pinning^{34,35}. As discussed above, minor Cu addition can obviously improve the Mg¹¹B₂ grain crystallization and reduce the amount of MgO impurity. Hence, improved grain connectivity and higher J_c at low fields is obtained in Cu doped Mg¹¹B₂ samples. On the other hand, minor Cu addition can also lead to the grain growth, implying that grain boundary pinning becomes weakened in Cu doped sample compared to undoped one. Moreover, more MgO impurity is formed in un-doped samples and some of them with proper size can also serve flux pinning centers. Consequently, better J_c performance at high fields is expected in undoped samples. From Table 1, one can see that the value of J_c and H_{irr} is increasing with the increasing sintering holding time. Besides, compared to previous studies²⁰, the J_c value is higher while the sintering time is shorter due to the state of ¹¹B which has

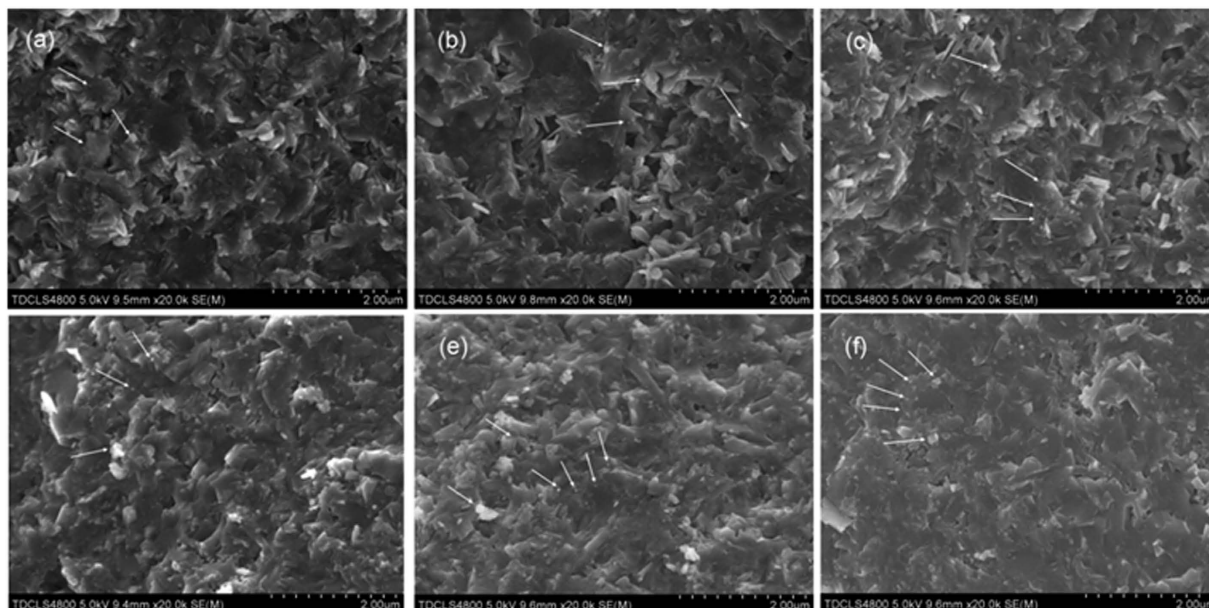


Figure 5. SEM images for the un-doped sintered for (a) 5 h, (b) 10 h, (c) 15 h, and the Cu-doped Mg^{11}B_2 samples sintered at (d) 5 h, (e) 10 h, (f) 15 h.

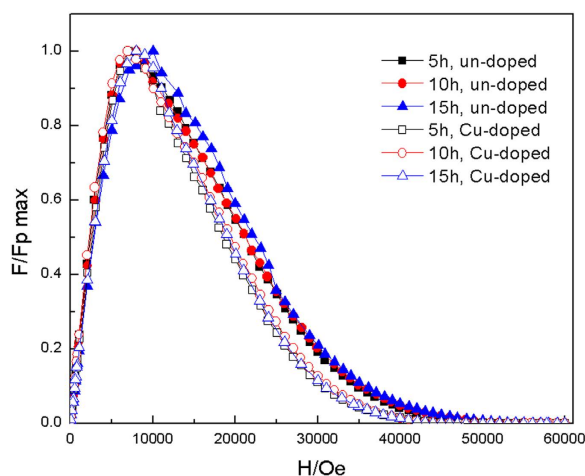


Figure 6. Normalized flux pinning force density as a function of applied magnetic field for the Mg^{11}B_2 samples.

smaller size and more activity. These advantages can accelerate the reaction rate and reduce the the raw materials exposure to oxygen, so it's beneficial to refine the grains and get much purer samples. On the whole, the un-doped sample for 15 h possesses the optimal performance in superconductivity. In order to manifest the cause, we have accomplished the following measurement.

The SEM images of un-doped and Cu-doped Mg^{11}B_2 samples are illustrated in Fig. 5. From the SEM images, the size of MgB_2 grains is larger in the Cu doped samples (about 600 ~ 800 nm) than that of un-doped samples (about 500 ~ 600 nm) and their individual grains with clear shape are easier to distinguish. In addition, the degree of crystallinity of Cu-doped samples is better than un-doped samples. These results indicate that slight Cu addition has a positive effect on the growth of grain and the improvement of crystallinity, which can enhance grain connectivity. And therefore, the J_c value of Cu-doped samples was improved at low field. The oxide particles, as the main impurities, are marked by the white arrows in these SEM images so that they can be recognized clearly. One can see that mass of oxide particles can be observed in sintered samples, especially in undoped samples. As holding time prolongs, the amount of these oxide particles gradually increase, consistent with the XRD results. It is explained that as the holding time increases, More MgO impurity can form for the reason that Mg further reacts with the trace oxygen in flowing Ar protective gas. Due to the small size of our Mg^{11}B_2 bulks ($\Phi 5 \times 1.5$ mm), even the trace oxygen in the flowing Ar protective gas can result in relatively large amount of MgO impurity. Observing carefully, one can also see that the size of MgO particles became smaller and their distribution became more

homogeneous with the extended holding time. It is worth noting that these small MgO particles may serve as the flux pinning centers as their size is comparable to the coherent length of pure MgB₂.

Figure 6 shows the normalized pinning force $F/F_{p,max}$ of Mg¹¹B₂ samples in magnetic field. One can see that the pinning peaks of un-doped samples moved to high field with the increasing holding time. This result suggests that the pinning force in the un-doped samples increases as the sintering time prolongs. Combined with the results above (as shown in the Fig. 5a–c), it is explained that there are more MgO impurity with the size comparable to the coherence length of MgB₂ in the un-doped samples, which is helpful to get and establish more pinning centers³⁶.

Conclusions

In present work, the Mg¹¹B₂ samples were synthesized by low-temperature sintering. The value of J_c of un-doped samples at high fields is higher than Cu-doped ones, whereas Cu-doped samples exhibit better J_c performance at low fields. Minor Cu addition can significantly promote the growth of Mg¹¹B₂ grains as well as decrease the amount of MgO impurity. Consequently, higher sintering density and improved grain connectivity are obtained in Cu doped Mg¹¹B₂ samples, which contribute to the better J_c performance at low fields. On the other hand, larger grain size and less MgO impurity can also decrease the flux pinning centers, and thus result in the lower J_c at high fields. For un-doped samples, unobvious growth of grain size and more volume fraction of MgO brought about the increase of flux pinning centers, hence, the un-doped samples show higher J_c performance at high field.

References

- Nakagawa, N. *et al.* Superconductivity at 39 K in magnesium diboride. *Nature* **410**, 63–64 (2001).
- Kim, J. H. *et al.* The doping effect of multiwall carbon nanotube on MgB₂/Fe superconductor wire. *J. Appl. Phys.* **100**, 013908 (2006).
- Yeoh, W. K. *et al.* Improving flux pinning of MgB₂ by carbon nanotube doping and ultrasonication. *Supercond. Sci. Technol.* **19**, L5–L8 (2006).
- Nath, M. & Parkinson, B. A. A simple sol-gel synthesis of superconducting MgB₂ nanowires. *Adv. Mater.* **18**, 1865–1868 (2006).
- Jha, A. K. & Khare, N. Single-crystalline superconducting MgB₂ nanowires. *Supercond. Sci. Technol.* **22**, 075017 (2009).
- Fujii, H. & Ozawa, K. Critical temperature and carbon substitution in MgB₂ prepared through the decomposition of Mg(BH₄)₂. *Supercond. Sci. Technol.* **23**, 125012 (2010).
- Kang, W. N. *et al.* MgB₂ superconducting thin films with a transition temperature of 39 Kelvin. *Science* **292**, 1521–1523 (2001).
- Hossain, M. S. A. *et al.* The enhanced J_c and B_{ir} of *in situ* MgB₂ wires and tapes alloyed with C₄H₆O₅ (malic acid) after cold high pressure densification. *Supercond. Sci. Technol.* **22**, 095004 (2009).
- Li, G. Z. *et al.* Critical current densities and n -values of MgB₂ strands over a wide range of temperatures and fields. *Supercond. Sci. Technol.* **25**, 025001 (2012).
- Hishinuma, Y. *et al.* Microstructure and superconductivity of Cu addition MgB₂ wires using Mg₂Cu compound as additional source material. *Supercond. Sci. Technol.* **19**, 1269–1273 (2006).
- Singh, K. *et al.* Effect of Cu doping in MgB₂ superconductor at various processing temperatures. *Physica C* **450**, 124–128 (2006).
- Noda, T., Takeuchi, T. & Fujita, M. Induced activity of several candidate superconductor materials in a tokamak-type fusion reactor. *J. Nucl. Mater.* **329–333**, 1590–1593 (2004).
- Boutboul, T., Le-Naour, S. & Leroy, D. Critical Current Density in Superconducting Nb-Ti Strands in the 100 mT to 11 T Applied Field Range. *IEEE Trans. Appl. Supercon.* **17**, 1184–1187 (2006).
- Xu, X., Sumption, M. D. & Collings, E. W. A model for phase evolution and volume expansion in tube type Nb₃Sn conductors. *Supercond. Sci. Technol.* **26**, 075015 (2013).
- Xu, X. C., Sumption, M. D. & Peng, X. Internally Oxidized Nb₃Sn Strands with Fine Grain Size and High Critical Current Density. *Adv. Mat.* **27**, 1346–1350 (2015).
- Mooring, E. P., Monahan, J. E. & Huddleston, C. M. Neutron cross sections of the boron isotopes for energies between 10 and 500 keV. *Nucl. Phys.* **82**, 16–32 (1966).
- Hinks, D. G. & Jorgensen, J. D. The isotope effect and phonons in MgB₂. *Physica C* **385**, 98–104 (2003).
- Choi, H. J., Cohen, M. L. & Louie, S. G. Anisotropic Eliashberg theory of MgB₂: T_c, isotope effects, superconducting energy gaps, quasiparticles, and specific heat. *Physica C* **385**, 66–74 (2003).
- Pitt, M. P. *et al.* *In situ* neutron diffraction study of the deuteration of isotopic Mg¹¹B₂. *J. Phys. Chem. C* **115**, 22669–22679 (2011).
- Hishinuma, Y. *et al.* Microstructure and superconducting properties of Cu addition MgB₂ multifilamentary wires using boron isotope powder as the boron source material. *Phys. Procedia* **36**, 1486–1491 (2012).
- Lu, J. *et al.* Low-temperature synthesis of superconducting nanocrystalline MgB₂. *J. Nanomater.* **2010**, 191058 (2010).
- Yamamoto, A. *et al.* Reactivity of carbides in synthesis of MgB₂ bulks. *Physica C* **445–448**, 801–805 (2006).
- Yamamoto, A. *et al.* Improved critical current properties observed in MgB₂ bulks synthesized by low-temperature solid-state reaction. *Supercond. Sci. Technol.* **18**, 116–121 (2005).
- Ma, Z. Q. & Liu, Y. C. The varied kinetics mechanisms in the synthesis of MgB₂ from elemental powders by low-temperature sintering. *Mater. Chem. Phys.* **126**, 114–117 (2011).
- Ma, Z. Q., Liu, Y. C. & Gao, Z. M. The synthesis and grain connectivity of lamellar MgB₂ grains by Cu-activated sintering at low temperature. *Scripta Materialia* **63**, 399–402 (2010).
- Ma, Z. Q. *et al.* The mechanism of accelerated phase formation of MgB₂ by Cu-doping during low-temperature sintering. *Mater. Res. Bull.* **44**, 531–537 (2009).
- Shi, Q. Z. *et al.* Phase formation process of bulk MgB₂ analyzed by differential thermal analysis during sintering. *J. Alloy. Compd.* **458**, 553–557 (2008).
- Bean, C. P. Magnetization of hard superconductors. *Phys. Rev. Lett.* **8**, 250–253 (1962).
- Zhao, Q. *et al.* Characteristic and synthesis mechanism of MgB₂ nanoparticles in solid-state reactive sintering. *J. Alloy. Compd.* **470**, 443–447 (2009).
- Ma, Z. Q. *et al.* The enhancement of J_c in nano SiC-doped MgB₂ superconductors rapidly synthesized by activated sintering at low-temperature. *Scripta Mater.* **61**, 836–839 (2009).
- Ma, Z. Q. *et al.* Effect of Cu addition in reduction of MgO content for the synthesis of MgB₂ through sintering. *J. Alloy. Compd.* **471**, 105–108 (2009).
- Yamamoto, A. *et al.* Improved critical current properties observed in MgB₂ bulks synthesized by low-temperature solid-state reaction. *Supercond. Sci. Technol.* **18**, 116–121 (2005).
- Ye, S. J. *et al.* Enhancing the critical current properties of internal Mg diffusion-processed MgB₂ wires by Mg addition. *Supercond. Sci. Technol.* **25**, 125014 (2012).

34. Shi, Z. X. *et al.* Doping effect and flux pinning mechanism of nano-SiC additions in MgB₂ strands. *Supercond. Sci. Technol.* **24**, 065015 (2011).
35. Shi, Z. X. *et al.* Anisotropic connectivity and its influence on critical current densities, irreversibility fields, and flux creep in *in situ* processed MgB₂ strands. *Supercond. Sci. Technol.* **23**, 045018 (2010).
36. Ma, Z. Q. *et al.* MgB₂ superconductors with abnormally- improved J_c sintered after autoxidation of milled original powders, *J. Appl. Phys.* **106**, 113911 (2009).

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Author Contributions

Z.M. and Y.L. designed the experimental scheme. F.C. prepared the samples and did most of the characterizations. M.S.A.H. helped with the experiment and data analysis and M.S. provided the boron powder.

Additional Information

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