Vol 17 No 3, March 2008
1674-1056/2008/17(03)/1124-06
Chinese Physics B
© 2008 Chin. Phys. Soc.
and IOP Publishing Ltd

Rapid preparation of $Mg(B_{1-x}C_x)_2$ superconductor using hybrid microwave method*

Guo Juan(郭 娟), Dong Cheng(董 成)†, Gao Hong(高 红), Wen Hai-Hu(闻海虎), Yang Li-Hong(杨立红), Zeng Fu(曾 富), and Chen Hong(陈 红)

National Laboratory for Superconductivity, Institute of Physics, Chinese Academy of Sciences, Beijing & National Laboratory for Condensed Matter Physics, Beijing 100080, *China*

(Received 26 March 2007; revised manuscript received 11 October 2007)

The crystal structure and the superconductivity for samples $Mg(B_{1-x}C_x)_2$ ($0 \leq x \leq 0.09$) prepared by a hybrid microwave synthesis have been investigated. The starting material $B_{10}C$ is also obtained by using the microwave method. The carbon can distribute uniformly in the $Mg(B_{1-x}C_x)_2$ samples because boron and carbon are mixed on an atomic scale in the staring material $B_{10}C$. The dependences of both lattice parameters and superconducting transition temperature T_c on carbon content accord with those reported in the literature. The upper critical field H_{c2} at 20 K can be enhanced from about 4.3 T for $x = 0$ to 10 T for $x = 0.05$. The critical current density J_c of $Mg(B_{0.95}C_{0.05})_2$ is 1.05×10^4 A/cm^2 at 20 K and 1 T.

Keywords: microwave synthesis, MgB_2 superconductor, carbon doping
PACC: 7460E, 7460J, 7470J

Since the discovery of its superconductivity, MgB_2[1] has aroused the interest of the researchers worldwide, for its critical temperature T_c has been the highest among simple binary compounds up to now. In addition to its high T_c, MgB_2 has other advantages in practical applications such as low cost of the raw materials, high upper critical field (H_{c2}), and critical current density (J_c) obtainable by chemical doping.[2–4] The pioneer research on carbon-doping at the boron sites was reported by Paranthaman *et al.*[5] The carbon doping into MgB_2 can lead to a gradual decline in T_c up to $x = 0.1$, beyond which T_c drops dramatically.[6] With the increase of carbon content, the lattice parameter a decreases linearly, while the lattice parameter c is virtually unchanged.[7] Senkowicz *et al* have obtained a linear relationship between the a-axis length and carbon content x by summarizing the results in Ref.[8]. The H_{c2} ($T = 0$) of $Mg(B_{1-x}C_x)_2$ wire reported by Wilke *et al*[9] can be raised in a field of 5 T, with 1% C substituted for B. The J_c of bulk MgB_2 samples can be improved by 1 to 2 orders of magnitude by the carbon doping.[10,11] Generally, for the application of superconductors, it is worthwhile to study the effect of carbon doping on the crystal structure and the superconductivity of $Mg(B_{1-x}C_x)_2$, especially, with lower carbon contents ($x < 0.1$).

At the early stage, the starting materials were usually pure Mg, amorphous B and C powders to prepare carbon-doped MgB_2. As the carbon and boron cannot be mixed on an atomic scale, the inhomogeneous and incomplete carbon incorporation usually appears.[12] Ribeiro *et al*[13] have reported that carbon can be uniformly substituted for boron by using B_4C as a precursor. From the B–C phase diagram,[12] the stable binary compound with a maximum atom ratio of B : C is $B_{10}C$. In order to investigate the lower carbon doping level in MgB_2 ($x < 0.1$ for $Mg(B_{1-x}C_x)_2$), the $B_{10}C$ is used as a carbon source in this paper.

Usually, the $Mg(B_{1-x}C_x)_2$ bulk samples are prepared in sealed tantalum and quartz tubes or by high pressure sintering.[5,14] Although these methods are very useful, they have some shortcomings for repetitive manufacturing due to the high cost of energy and materials. In recent years, the microwave processing has been used extensively for material synthesis, for it is clean, time saving and high energy efficiency.[15,16] We have successfully prepared the MgB_2 superconductor by a hybrid microwave synthesis,[17] and here in the present study we adopt this technique to synthe-

*Project supported by the National Natural Science Foundation of China (Grant Nos 20271052 and 20571083) and the National Basic Research Program of China (Grant No 2006CB601004).
†Corresponding author. E-mail: chengdon@aphy.iphy.ac.cn

size $Mg(B_{1-x}C_x)_2$. The dependences of crystal structures and superconductivity on carbon-doped MgB_2 are investigated.

Samples $Mg(B_{1-x}C_x)_2$ ($0 \leq x \leq 0.09$) are prepared using stoichiometric magnesium powder, amorphous boron powder (with particle size $< 3\,\mu$m) and compound $B_{10}C$ as starting materials. The reaction equation can be written as follows: $Mg+2xB_{10}C+(2-22x)B = Mg(B_{1-x}C_x)_2$. The starting materials are thoroughly mixed in a glass bottle by wobbling, and then pressed into pellets ($\Phi 20\times 2$ mm) at a pressure of 15 MPa. The flowing Ar gas is used to prevent the samples from being oxidated in the microwave heating process. The detailed experimental method used has been described elsewhere[16] except for the heating medium that has been changed from CuO to SiC powder. The power and the duration of microwave heating are respectively 560 W and 6–10 minutes for all samples.

The compound $B_{10}C$ is obtained from the mixture of amorphous boron powder and graphite powder with a mole ratio of B : C = 10 : 1. The reagent is mixed in ball mill (QM-1SP04) for four hours. The samples are prepared also by hybrid microwave synthesis and the power and the duration of microwave heating are 800 W and 8 minutes respectively.

The prepared samples are characterized by powder x-ray diffraction (XRD) and scanning electron microscopy (SEM). The powder x-ray diffraction data are collected by using an M18X-AHF rotating-anode diffractometer with the Cu Kα radiation. Lattice parameters are calculated using a least-square method with Powder X program.[18] The grain morphology and its microstructure are obtained by using a scanning electron microscope (XL30 S-FEG). The temperature dependence of electrical resistivity is measured by a standard four-probe method with a voltage resolution of 10^{-7} V. The dependences of diamagnetic moment and resistivity on temperature under different given applied fields are obtained by using a SQUID magnetometer (Quantum Design MPMS-5) and an Oxford cryogenic system (Maglab-12) respectively. The magnetic hysteresis loops (MHLs) are also measured by a SQUID magnetometer. The critical current density J_c is calculated from the magnetic hysteresis data based on the Bean model by using a formula for the rectangularly shaped samples.[19]

The XRD pattern of sample $B_{10}C$ is displayed in Fig.1. The broad peaks in this pattern indicate that the sizes of the $B_{10}C$ crystallites are quite small, which is due to the short reaction time and the amorphous boron starting materials in preparation. The diffraction peaks can be indexed by a hexagonal lattice with $a = 0.56076$ nm and $c = 1.21899$ nm. This structure is isostructural with that of B_4C-phase in the B–C phase diagram.[12] Therefore, $B_{10}C$ is not a new phase but a boron-rich solid solution of the B_4C phase.

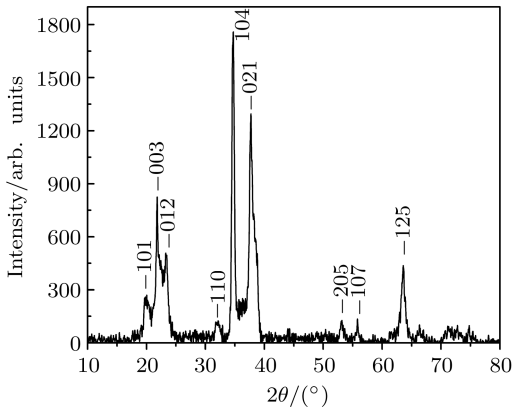


Fig.1. XRD pattern for sample $B_{10}C$.

Figure 2 shows the XRD patterns for samples $Mg(B_{1-x}C_x)_2$ ($0 \leq x \leq 0.09$). The phase analysis reveals that the major phase has a AlB_2 structure. The impurity peaks can be attributed to MgO and MgB_4. The minor phase MgB_4 appears only in three

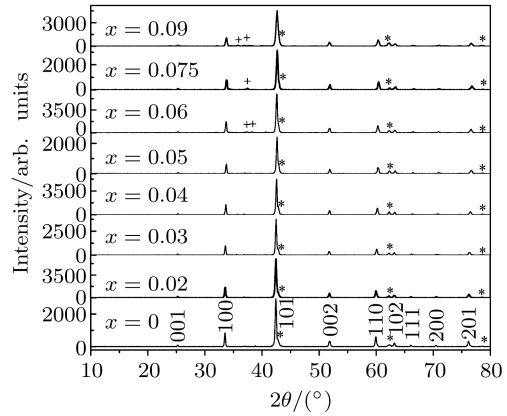


Fig.2. XRD patterns for samples $Mg(B_{1-x}C_x)_2$ ($0 \leq x \leq 0.09$, where the mark * refers to MgO and + refers to MgB_4).

samples. The lattice parameters are calculated and plotted in Fig.3 with carbon content varying from 0 to 0.09. While c-axis has little change in the carbon-doped samples, the lattice parameter a decreases linearly with the increase of carbon content. The contraction of a-axis indicates that the atomic distance

shortens in the boron layers and the B–B bond become strong with the carbon content increasing. The interaction between Mg- and B-layers is barely influenced by the carbon doping.

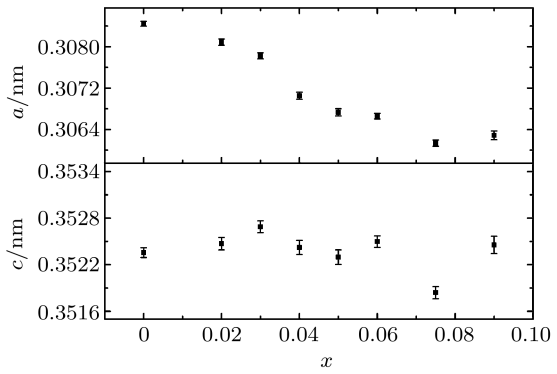


Fig.3. The values of lattice parameters a and c for $Mg(B_{1-x}C_x)_2$ ($0 \le x \le 0.09$) samples versus carbon content x.

According to the relationship $a = 3.08439 - 0.3153x$ reported by Senkowicz *et al*,[8] the carbon content x for samples $Mg(B_{1-x}C_x)_2$ can be calculated by using the a-axis length. Figure 4 shows the dependences of calculated and nominal carbon contents on the a-axis length. It can be seen that the calculated values are very close to the nominal ones except for the data of the sample with $x = 0.09$. It is clear that the carbon is successfully doped into the lattice and the carbon content x for samples $Mg(B_{1-x}C_x)_2$ can also be effectively controlled by the mole ratio of starting materials using the microwave synthesis.

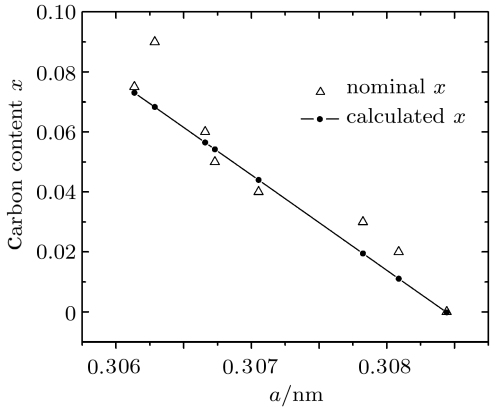


Fig.4. The nominal and calculated values of carbon content x versus a-axis length for samples $Mg(B_{1-x}C_x)_2$ ($0 \le x \le 0.09$).

The grain morphology and microstructure of samples are investigated with scanning electron microscopy. As shown in Fig.5, there is no significant difference in the crystallite appearances with the carbon content varying. For the samples with $x = 0$ and 0.05, the typical hexagonal-platelet crystallites can be seen and the edge length is about $0.5\,\mu$m (Figs.5(a),

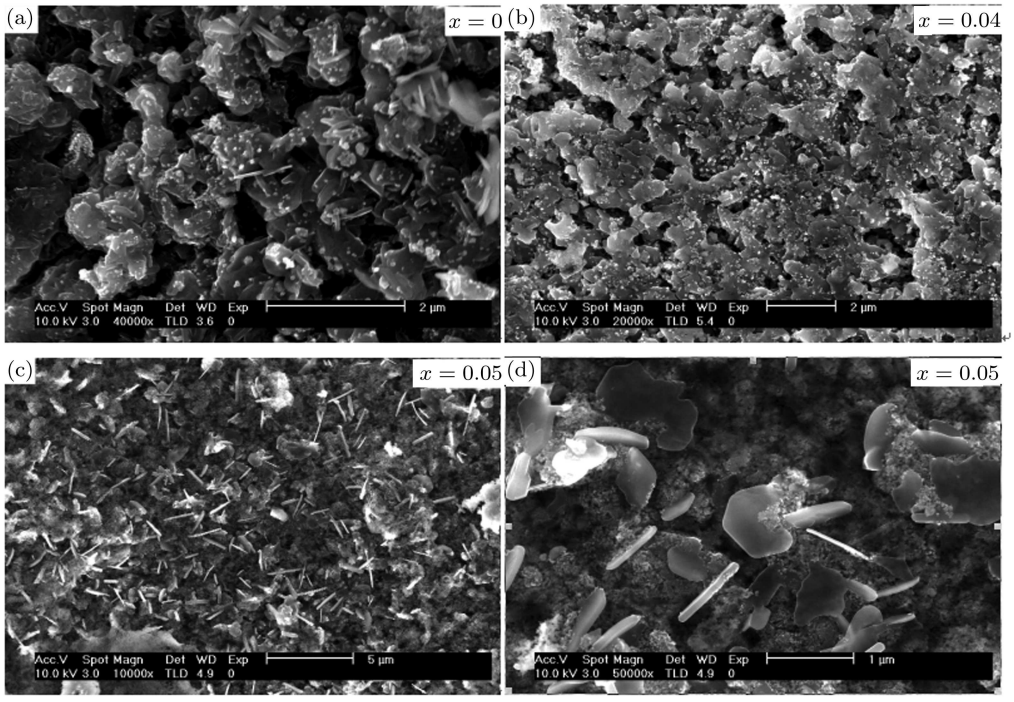


Fig.5. SEM micrographs for samples $Mg(B_{1-x}C_x)_2$ with the values of x being 0, 0.04 and 0.05.

5(c) and 5(d)). The sub-micrometre-sized ($\sim 0.1\,\mu$m) crystallites also appear in the sample with $x = 0.05$ (Fig.5(d)). For the sample with $x = 0.04$, the hexagonal-platelet crystallites adhere to each other and irregularly shaped crystallites are formed. The average size is in a range of 0.5–1 μm (Fig.5(b)).

The temperature dependence of resistivity for $Mg(B_{1-x}C_x)_2$ ($0 \le x \le 0.09$) is plotted in Fig.6(a). The curve of superconducting transition temperature T_c at $\rho = 0$ versus carbon content x is shown in Fig.6(b). It can be seen that with the increase of carbon content the T_c ($\rho = 0$) decreases almost linearly from 38.1 K for $x = 0$ to 32.0 K for $x = 0.09$. These results show that the substitute of carbon for boron may affect the uniformity of boron layer and suppress the superconductivity in MgB_2.

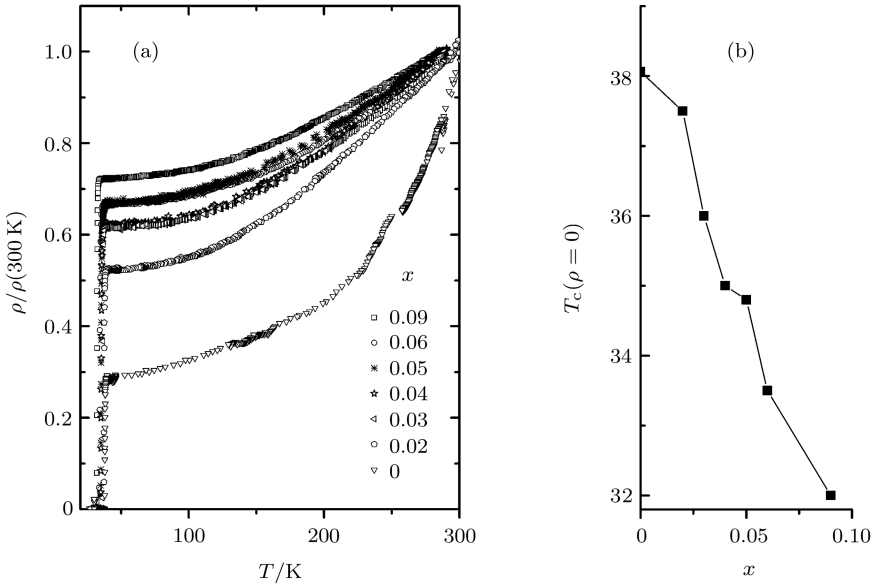


Fig.6. Dependence of resistivity on temperature (a) and dependence of T_c ($\rho = 0$) on carbon content x (b) for $Mg(B_{1-x}C_x)_2$ ($0 \le x \le 0.09$).

The upper critical field dependence on temperature, $H_{c2}(T)$, has been investigated for samples with $x = 0$ and 0.05. The H_{c2} values have been respectively determined from susceptibility data for MgB_2 and resistivity data for $Mg(B_{0.95}C_{0.05})_2$, which is simply due to the availability of the measuring instruments. The $m - T$ and $\rho - T$ curves measured under several given applied fields are displayed in Figs.7(a) and 7(b). It

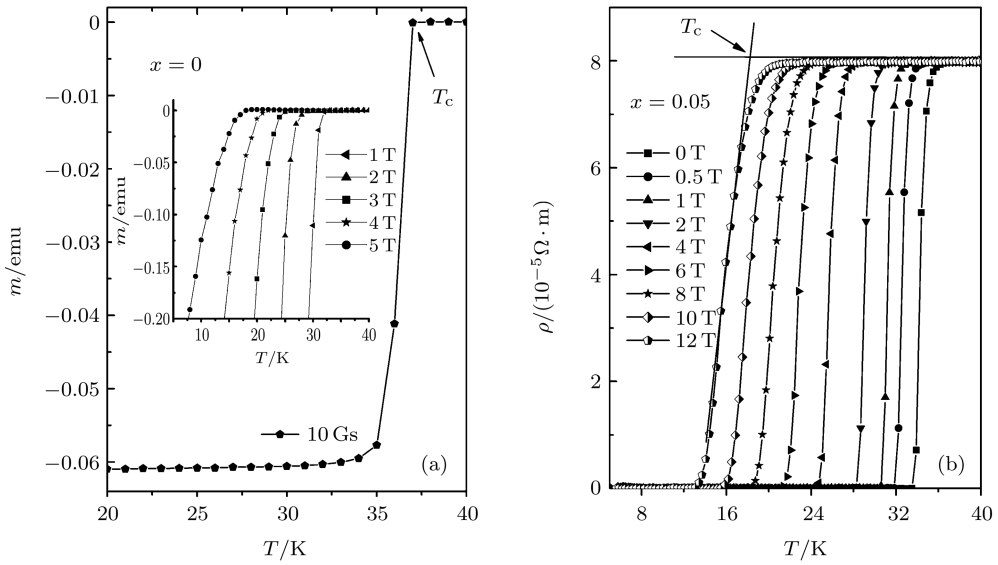


Fig.7. Temperature dependences of diamagnetic moment for MgB_2 (a) and resistibility for $Mg(B_{0.95}C_{0.05})_2$ (b) under different applied fields.

can be seen that the values of T_c for both samples decrease with the increase of applied field. The onset criteria used to determine the values of T_c from ρ–T and m–T curves are illustrated in the figures. Figure 8 shows the H_{c2}–T curves based on the T_c under different applied fields. It can be seen that the H_{c2} at 20 K is enhanced from about 4.3 T for $x = 0$ to 10 T for $x = 0.05$. Although the methods to determine the values of T_c for MgB_2 and $Mg(B_{0.95}C_{0.05})_2$ are different, the discrepancy caused by the different methods is not significant.[20] In this figure, it is still obvious that the H_{c2} is improved by carbon doping into MgB_2 superconductor. The result of H_{c2} (T) for sample $Mg(B_{0.95}C_{0.05})_2$ is very close to that of samples with the same carbon content, synthesized at a high pressure (HP) or an ambient pressure (AP) in an Ar atmosphere.[14]

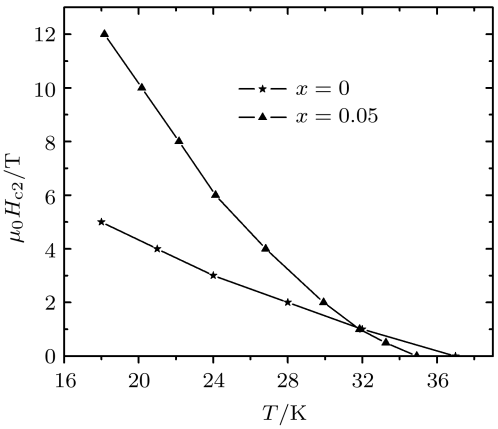


Fig.8. $\mu_0 H_{c2}$–T curves of samples with $x = 0$ and 0.05.

The enhanced H_{c2} shows that the substitution of carbon for boron in MgB_2 samples does significantly increase the pinning. From Fig.5, the small grain sizes in carbon doping samples generate more grain boundaries as effective pinning centres.[4]

Figure 9(a) shows the MHLs for sample $Mg(B_{0.95}C_{0.05})_2$ at temperatures of 5, 10, 15, 20 and 25 K and at applied fields ranging from 0 to 5 T. The J_c(H) calculated from MHLs is plotted in Fig.9(b). It can be seen that the J_c decreases with the rise of temperature and its value is 1.05×10^4 A/cm^2 at 20 K and 1 T. Considering the porosity caused by the volatilization of Mg and the oxidation of C in the synthesis process, it is possible to raise J_c of the as-prepared samples by subsequent pressing and high-temperature sintering to make the samples denser.

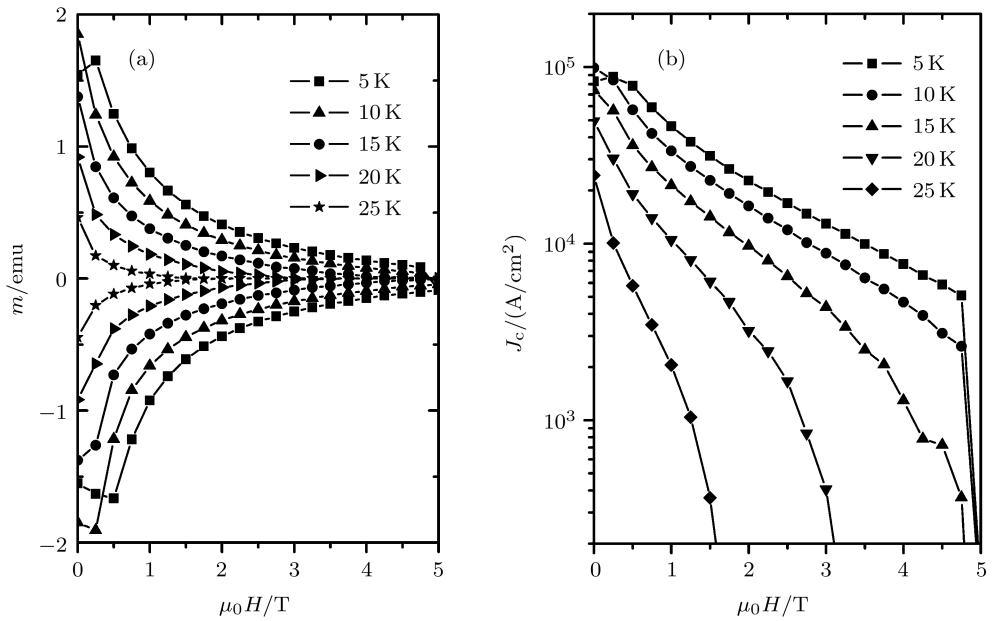


Fig.9. Magnetic hysteresis loops ($H > 0$) (a) and J_c–$\mu_0 H$ curves (b) for sample $Mg(B_{0.95}C_{0.05})_2$.

From all the results above, it is clear that both the crystal structure and the superconductivity of samples $Mg(B_{1-x}C_x)_2$ ($0 \le x \le 0.09$) prepared by the microwave synthesis accord with those reported in the literature. The present microwave method can promote homogeneous distribution of carbon in sam-

ples because the carbon and boron are mixed on an atomic length scale in the staring material $B_{10}C$. In addition, this hybrid microwave synthesis is simple and facile compared with the method using sealed tubes, so it can be used in the repetitive manufacturing of $Mg(B_{1-x}C_x)_2$ superconductor. This technique is now utilized to prepare raw materials for making the carbon-doped MgB_2 tapes, and the experimental study is underway in our laboratory.

In summary, The $B_{10}C$ compound can be obtained by a hybrid microwave synthesis from boron and graphite powders. The bulk samples $Mg(B_{1-x}C_x)_2$ ($0 \leq x \leq 0.09$) are prepared by the same method using $B_{10}C$ as a carbon source. Using this hybrid microwave method, the carbon content of samples can be easily controlled by adjusting the mole ratio of starting materials, and homogeneous distribution of carbon in samples is guaranteed by the atomic-length-scale mixing of boron and carbon in the starting material $B_{10}C$. The simple microwave synthesis method has potential applications in the repetitive manufacturing of bulk $Mg(B_{1-x}C_x)_2$ superconductors.

References

[1] Nagamatsu J, Nakagawa N, Muranaka T, Zenitani Y and Akimitsu J 2001 *Nature* **410** 63

[2] Zhao Y, Feng Y, Cheng C H, Zhou L, Wu Y, Machi T, Fudamoto Y, Koshizuba N and Murakami M 2001 *Appl. Phys. Lett.* **79** 1154

[3] Li Q, Gu G D and Zhu Y 2003 *Appl. Phys. Lett.* **82** 2103

[4] Yamada H, Hirakawa M, Kumakura H, Matsumoto A and Kitaguchi H 2004 *Appl. Phys. Lett.* **84** 1728

[5] Paranthaman M, Thompson J R and Christen D K 2001 *Physica* C **355** 1

[6] Kazakov S M, Puzniak R, Rogacki K, Mironov A V, Zhigadlo N D, Jun J, Soltmann Ch, Batlogg B and Karpinski J 2005 *Phys. Rev.* B **71** 024533

[7] Bharathi A, Balaselvi S J, Kalavathi S, Reddy G L N, Sastry V S, Hariharan Y and Radhakrishnan T S 2002 *Physica* C **370** 211

[8] Senkowicz B J, Giencke J E, Patnaik S, Eom C B, Hellstrom E E and Larbalestier D C 2005 *Appl. Phys. Lett.* **86** 202502

[9] Wilke R H T, Bud'ko S L, Canfield P C, Finnemore D K, Suplinskas R J and Hannahs S T 2004 *Phys. Rev. Lett.* **92** 217003

[10] Cheng Z H, Shen B G, Zhang J, Zhang S Y, Zhao T Y and Zhao H W 2002 *J. Appl. Phys.* **91** 7125

[11] Wang X L, Soltanian S, James M, Qin M J, Horvat J, Yao Q W, Liu H K and Dou S X 2004 *Physica* C **408–410** 63

[12] Wilke R H T, Bud'ko S L, Canfield P C, Finnemore D K, Suplinskas R J and Hannahs S T 2005 *Physica* C **424** 1

[13] Ribeiro R A, Bud'ko S L, Petrovic C and Canfield P C 2003 *Physica* C **384** 227

[14] Yuan G Q, Xu X N, Wang Z H, Lu D W and Jin X 2005 *Solid State Commun.* **135** 352

[15] Agrawal D K 1998 *Curr. Opin. Solid State Mater. Sci.* **3** 480

[16] Guo J, Dong C, Yang L H and Fu G C 2005 *J. Solid State Chem.* **178** 58

[17] Dong C, Guo J, Fu G C, Yang L H and Chen H 2004 *Supercond. Sci. Technol.* **17** L55

[18] Dong C 1999 *J. Appl. Cryst.* **32** 838

[19] Zheng D N, Ali S, Hamid H A, Eastell C, Goringe M and Hampshire D P 1997 *Physica* C **291** 49

[20] Huang X S, Mickelson W, Regan B C and Zettl A 2005 *Solid State Commun.* **136** 278