Synthesis of Mg(B$_{1-x}$C$_x$)$_2$ Powders

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Abstract

We have synthesized bulk Mg(B$_{1-x}$C$_x$)$_2$ from a mixture of elemental Mg, B, and the binary compound B$_4$C. Carbon incorporation was dramatically improved by a two step reaction process at an elevated temperature of 1200 °C. This reaction process results in a solubility limit near $x \sim 0.07$. We found that impurities in the starting B cause an additive suppression of $T_c$. We combine these data with $T_c$ and $H_{c2}(T=0)$ data from CVD wires as well as plasma spray synthesized powders and present a unifying $H_{c2}$ and $T_c$ versus $x$ plot.

Key words: MgB$_2$, carbon doping, upper critical field
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1 Introduction

Superconductivity in MgB$_2$ near 40 K [1] has attracted much interest due to its potential for applications in the 20-30 K range. The low upper critical field [2] and high anisotropy ratio, $\gamma=H_{c2}^{ab}/H_{c2}^{ab}$ [3,4,5], of pure MgB$_2$, limit its potential usefulness [6]. Carbon doping of MgB$_2$ has been shown to be an effective method for enhancing $H_{c2}$ [7,8,9] while simultaneously decreasing the anisotropy ratio by increasing $H_{c2}^{ab}$ more rapidly than $H_{c2}^{ab}$ [10,11]. Carbon doped MgB$_2$ filaments require high reaction temperatures which lead to large grain sizes and poor $J_c$ values, in spite of the enhancements in $H_{c2}$ [12]. Reports of successful fabrication of superconducting wire using powder-in-tube processing [13,14], coupled with the fact that $J_c$ values in powder samples can readily be increased by the addition of various particles [15,16,17,18] motivate
a desire for synthesizing single phase carbon doped MgB$_2$ powder. Carbon doped bulk polycrystalline MgB$_2$ with approximately 10% carbon incorporation has previously been synthesized by mixing elemental Mg and the binary B$_4$C [19,20]. Systematic carbon doping of Mg(B$_{1-x}$C$_x$)$_2$ with x<0.10 has been achieved in single crystals [8,21] and polycrystalline wires fabricated by chemical vapor deposition (CVD) [7,12]. In this paper we explore the possibility of preparing Mg(B$_{1-x}$C$_x$)$_2$ with x<0.10 using B$_4$C as the carbon source.

2 Experimental Methods

Powder samples of Mg(B$_{1-x}$C$_x$)$_2$ were prepared in a two step process. First, stoichiometric mixtures of distilled Mg, elemental B, and the binary compound B$_4$C were reacted for 48 hours at 1200 °C. The resultant sample was then reground in acetone, pressed into a pellet, and re-sintered for an additional 48 hours at 1200 °C. Two different batches were made. The first with 0.995 purity B (metals basis) from Alpha Aesar, and the second with 0.9997 purity isotopically enriched $^{11}$B from Eagle Picher. The three main impurities in the 0.995 purity B are C, Si, and Fe, which have relative atomic abundances of 0.25% and 0.20%, and 0.10% respectively. The isotopically enriched $^{11}$B contained 0.02% Ta, 0.001% Cu, and 0.001% Fe. Samples made with isotopically enriched $^{11}$B were shown to have a higher residual resistivity ratio (RRR) than samples made with nominal 0.9999 purity B, indicating the isotopic enrichment process yields perhaps the purest boron available [22]. B$_4$C from Alpha Aesar was used as the carbon source in both runs. The B$_4$C had a nominal purity of 0.994 metals basis with the two primary impurities being Si and Fe, which occur in relative abundances of 0.37% and 0.074% respectively, values similar to those in the 0.995 purity B. Since impurities in the boron have been shown to suppress T$_c$ [22], two differing boron purities were used to examine the effects of the starting boron purity on the T$_c$ and H$_c2$(T=0) values in carbon doped MgB$_2$. We found it necessary to use multiple reaction steps to incorporate the carbon as uniformly as possible. To avoid confusion regarding the meaning of x in Mg(B$_{1-x}$C$_x$)$_2$, we will henceforth refer to the nominal carbon content as x$_n$ and the inferred carbon content after the m-th reaction step as x$_{im}$.

Powder x-ray diffraction (XRD) measurements were made at room temperature using CuK$_\alpha$ radiation in a Rigaku Miniflex Diffractometer. A silicon standard was used to calibrate each pattern. Lattice parameters were determined from the position of the MgB$_2$ (002) and (110) peaks. DC magnetization measurements were performed in a Quantum Design MPMS-5 SQUID magnetometer. Transport measurements were done using a four probe technique, with platinum wires attached to the samples with Epotek H20E silver epoxy. Resistance versus temperature in applied fields up to 14 T were carried out in
a Quantum Design PPMS-14 system and resistance versus field was measured up to 32.5 T using a lock-in amplifier technique in a resistive DC magnet at the National High Magnetic Field Laboratory in Tallahassee, Florida.

3 Results and Discussion

Using the lower purity boron, we reacted a sample with nominal carbon content of $x_n=0.05$ for 48 hours at 1200 °C. The carbon content can be estimated by the shift of the x-ray (110) peak position relative to that of a nominally pure MgB$_2$ sample made under the same conditions [7,20]. Although the B$_4$C is a different B source than that used for the reference sample, the 0.994 purity B$_4$C and 0.995 purity B contain similar concentrations of impurity phases, and we cautiously proceed with estimates of the carbon content ignoring minor differences between boron sources. Indexing of the (110) peak for the pure sample and that containing a nominal carbon content of $x_n=0.05$ yielded an inferred carbon level after this first reaction step of approximately $x_{i1}=0.031$. In order to ensure the carbon was fully incorporated and uniformly distributed within this sample, it was reground in acetone, pressed into a pellet, and sintered for an addition 48 hours at 1200 °C. The subsequent sample showed a further increase in the (110) peak position (Figure 1) which yielded an inferred carbon content of $x_{i2}=0.069$. This sample also showed decrease in $T_c$ (Figure 2), which is consistent with more carbon being incorporated in the structure. In addition to shifting to higher $2\theta$, the (110) peak became sharper. The full-width-at-half-maximum (FWHM) decreased from 0.221° to 0.157° after the second sintering step. Therefore the second sintering step not only incorporated more carbon but it appears to have resulted in a more uniform carbon distribution. It should be noted that after the two sintering steps the FWHM values of the MgB$_2$ peaks were comparable to those of the Si standard, indicating we have achieved a fairly high level of homogeneity. It is also worth noting that whereas the (110) peak shifts and sharpens as a result of a second reaction step, the (002) peak does neither, having FWHM values comparable to, but slightly larger than, the neighboring Si (311) peak after both reaction steps. This indicates that the c-axis spacing and periodicity are particularly insensitive to this degree of carbon doping and/or disorder.

Whereas the $x_{i2}$ value exceeds the nominal value of $x_n=0.05$ in the starting material, the presence of MgB$_4$, as evidenced by strong peaks in the x-ray spectrum (Figure 3) may account for the discrepancy if we assume no carbon enters the MgB$_4$ structure. Comparison of the x-ray spectra for the single and two step reactions shows an increase in the intensity of the MgB$_4$ peaks after the second reaction step. This step was done without the addition of any extra Mg to compensate for potential Mg loss. It is possible that while sintering at 1200 °C, some Mg is driven out of the MgB$_2$ structure and this loss
results in conversion of MgB₂ to MgB₄, with the excess Mg forming MgO and possibly condensing on the walls of the tantalum reaction vessel during the quench. To determine whether or not Mg loss is responsible for the apparent increase in the carbon content, the second sintering step for a sample with nominal concentration $x_n=0.05$ was carried out in an atmosphere of excess Mg vapor. This sample exhibited a $T_c$ of 29.8 K and a shift in the (110) x-ray peak yielding an inferred carbon concentration of $x_i=0.050$ (Figure 4), consistent with the nominal concentration. Thus the apparent difference in carbon content for samples which undergo a second sintering step without the presence of excess Mg to compensate for Mg loss relative to those which undergo the second sintering step with excess Mg is presumably the result of a fixed amount of carbon being incorporated into a decreased amount of MgB₂. To avoid the potential creation of percolation networks of Mg within the samples we chose to perform the second sintering step without any additional Mg.

Using 0.995 purity boron and 0.994 purity B₄C, an entire series with nominal carbon levels of $x_n=0, 0.0125, 0.025, 0.035, 0.05,$ and $0.075$ was prepared using the two step reaction profile. The (002) and (110) x-ray peak positions for the entire series are plotted in figure 5. The (002) peak position is roughly constant for all carbon levels, consistent with the results found by Wilke et al. [7] and Avdeev et al. [20], which showed only a slight expansion along the c-axis for carbon doping levels up to $10\pm2\%$. The (110) peak position shifts towards higher $2\theta$ values as $x$ is increased up to $x_n=0.05$, at which point it appears to be saturated. Using the (110) peak position for the nominally pure sample as our standard, the inferred carbon concentrations for the entire series are $x_i=0, 0.01, 0.034, 0.044, 0.069,$ and $0.067$. The samples with carbon concentrations saturating near $x_i\sim0.07$ show an increase in the MgB₂C₂ phase as a function of the nominal carbon content (Figure 5b). Thus the excess carbon is precipitating out as MgB₂C₂.

Normalized magnetization measurements (Figure 6) confirm the highest two doping levels have incorporated roughly the same amount of carbon. Their transition temperatures all lie slightly below 28 K. Defining $T_c$ using a 2% screening criteria the $x_i=0.069$ and $0.067$ levels have $T_c$ values of 27.5 K and 27.8 K respectively. For these higher doping levels, the nominal concentrations did not yield systematic increases in carbon level, but the change in the a-lattice parameter and $T_c$ are consistent with one another; i.e. samples which apparently incorporated more carbon had smaller a-lattice parameters and lower $T_c$ values.

This saturation near $x_i=0.07$ is not entirely unexpected given the results of $10\pm2\%$ carbon incorporation using B₄C reported by Ribeiro et al. [19] and Avdeev et al. [20]. In optimizing the reaction, Ribeiro found that under certain conditions, $T_c$ values below the near 22 K reported for the optimal
24 hours at 1100 °C reaction could be attained, suggesting higher carbon content phases may be metastable. To test whether the saturation we observed was an effect due to the use of a two step reaction, as opposed to the single step employed by Ribeiro et al., we repeated their work, making a sample of nominal concentration Mg(B_{0.8}C_{0.2})_2 using only Mg plus B\textsubscript{4}C. This sample underwent an initial 48 hour reaction at 1200 °C to form the superconducting phase and a second sintering for 48 hours at 1200 °C. After the first 48 hours at 1200 °C we find a superconducting phase with T\textsubscript{c} near 22 K, and a lattice parameter shift which yielded inferred values of x\textsubscript{i}=0.092 slightly less than the x\textsubscript{i}=0.10 obtained by Ribeiro and coworkers using isotopically enriched \textsuperscript{11}B\textsubscript{4}C as the carbon source [20]. After the second sintering step, T\textsubscript{c} rises to 27.9 K. The (110) x-ray peaks shifted to lower 2\theta, yielding an inferred x\textsubscript{i}=0.065 (Figure 7). Although two reaction steps were used, no change in the FWHM of the (110) peak was observed. As in the case of the x\textsubscript{i}=0.075 sample, the decrease in carbon content could be due to carbon precipitating out in the form of MgB\textsubscript{2}C\textsubscript{2}. The relative intensity of the most prominent MgB\textsubscript{2}C\textsubscript{2} peak to that of MgB\textsubscript{2} approximately doubles going from the single step reaction to the two step reaction. In order to check if more carbon would be precipitated out in the form of MgB\textsubscript{2}C\textsubscript{2} by simply adding more sintering steps to the growth process an additional sample underwent a three step reaction: an initial 48 hours at 1200 °C to form the superconducting phase followed by two additional sintering steps of 48 hours at 1200 °C. After this third reaction step, the sample exhibited a T\textsubscript{c} of 27.9 K and the (110) peak position yielded an inferred carbon content of x\textsubscript{i}=0.064 (Figure 7). These values are comparable to our previous results with only two sintering steps. Thus the carbon content appears to saturate in the vicinity of an inferred carbon content of x\textsubscript{i}=0.065. The fact that saturation near x\textsubscript{i}=0.065 occurred for samples which had x\textsubscript{i} both above and below this level indicates that in equilibrium the solubility limit for 1200 °C reactions near 1 atm is in the range 0.065<x\textsubscript{i}<0.07.

Transport measurements were made in order to determine the upper critical field. An onset criteria was used in both resistance versus temperature and resistance versus field. Figure 8a plots resistance versus temperature in applied fields up to 14 T and figure 8b plots resistance versus field at temperatures down to 1.4 K for the sample with a carbon level of x\textsubscript{i}=0.069 (x\textsubscript{n}=0.05). The zero field resistive transition has a width of less than 1 K, but this significantly broadens as the strength of the applied field increases. The R vs. H measurements show a related broadening. For example, the width of the transition at 1.4 K is nearly 20 T wide. This should be compared to the 10 T wide, approximately linear transitions reported for 5.2% carbon doped filaments [12]. Optical images taken under polarized light show the superconducting grains in the powder sample are 5-10 \textmu m in size. In the case of the wire sample a majority of the grains are in the 1-5 \textmu m range [12]. We therefore ascribe the increased width of this transition to a combination of poor flux pinning due to the large grain size associated with the high reaction temperature as well
as to possible remaining inhomogeneities in carbon incorporation within the sample.

$H_{c2}$ curves for $x_{i2}=0.034$ and $x_{i2}=0.069$ along with a pure wire [2] and a carbon doped wire with an inferred carbon content of $x_i=0.052$ [7] are plotted in figure 9. The powder sample with $x_{i2}=0.034$ has a $T_c$ slightly less than that of the carbon doped wire with $x_i=0.052$ and an $H_{c2}(T=0)$ more than 5 T lower. This marked difference shows that for carbon doped samples made with differing nominal boron purities, $T_c$ alone is not a good caliper of $H_{c2}(T=0)$. The sample with inferred carbon content of $x_{i2}=0.069$ has a $T_c$ nearly 7 K below the aforementioned wire and an $H_{c2}(T=0)$ just above 30 T. Comparing the two powder samples to one another, we see an increase in the slope of $H_{c2}$ near $T_c$ for the higher doping level, which results in a higher $H_{c2}(T=0)$, consistent with our earlier findings [7,12].

Carbon has been shown to suppress $T_c$ at a rate of roughly 1 K/%C for up to 5% carbon substitution [12]. The magnetization and transport measurements indicate $T_c$ of the powder samples made with the 0.995 purity Alpha Aesar boron is also being suppressed at a rate of roughly 1 K/%C, but relative to the suppressed, near 37 K, transition temperature of the nominally pure sample. The suppressed transition temperature of the nominally pure MgB$_2$ sample lies approximately 2 K below results obtained using high purity natural boron wires [23]. MgB$_2$ made from lower purity boron has been shown to have lower transition temperatures [22]. In figure 10, a comparison of $T_c$ versus $|\Delta a|$ for carbon doped samples prepared with lower purity boron to carbon doped wires made with high purity boron shows the manifold associated with the impure boron powder is shifted downward by approximately 2 K for all carbon levels. To confirm that this difference is a result of the purity of the starting boron, a second set of two step process samples made with isotopically enriched $^{11}$B were measured. The results are included in figure 10. Also included is a set of carbon doped powders made by a plasma spray process [24]. The agreement between the CVD wires, plasma spray powders, and $^{11}$B samples shows that high purity boron in a variety of forms responds to carbon doping in a similar manner. These data also seem to indicate that there is some additional impurity in the 0.995 pure Alpha Aesar boron that is systematically suppressing $T_c$.

Figure 11 plots a comparison of the (002) and (110) x-ray peaks of pure MgB$_2$ using the three different purity levels of boron. The sample made with the nominal 0.995 purity boron shows a shift of the (110) peak to higher 2$\theta$ by 0.09°, which, if it were to be associated with carbon doping, would be consistent with carbon doping of approximately 1.8%. This level far exceeds the stated carbon impurity level of 0.25% in the 0.995 purity B as claimed in the certificate of analysis provided by Alpha Aesar. To check whether by using lower purity boron we have inadvertently doped with carbon to such a high
level, we measured the resistive onset of superconductivity in an externally applied 14 T field for the nominal pure MgB$_2$ using the 0.995 purity boron and compared the temperature with those attained for carbon doped fibers reported in reference [12]. MgB$_2$ fibers reacted at 1200 °C for 48 hours showed an onset of superconductivity in an externally applied magnetic field of 14 T at 10.2 K, 14.8 K, and 18.5 K for pure, 0.6%, and 2.1% carbon doping [12]. If the shift of the (110) peak in the nominally pure MgB$_2$ made from 0.995 purity boron were a result of inadvertent carbon doping, we would expect an onset of superconductivity in an applied 14 T field at a temperature between 15 K and 18 K. However, such a measurement yielded an onset near 13K indicating if carbon is present as an impurity, it is less than 0.6%, which consistent with the estimate provided by Alpha Aesar. Therefore the manifold of T$_c$ versus $|\Delta a|$ for the lower purity boron is shifted downward by some as of yet unidentified impurity associated with the Alpha Aesar boron.

H$_{c2}$ values were determined using an onset criteria in resistivity versus temperature and resistance versus field measurements. Pellets made using the isotopically enriched $^{11}$B lacked structural integrity and were unsuitable for transport measurements. Therefore we could only attain H$_{c2}$(T=0) values only for samples made from the CVD wires, plasma spray powders, and the 0.995 purity boron (Figure 12). For the dirtier, 0.995 purity powder, at a doping level of $x_{i2}=0.034$ the upper critical field agrees with the results of a carbon doped wire with an inferred carbon content of $x_i=0.038$ from reference [7]. At doping levels near $x_{i2}=0.065$, H$_{c2}$ values fall several Tesla below the manifold for ”clean” carbon doped samples. In carbon doped MgB$_2$, enhancement of H$_{c2}$ due to scattering effects [11,26] competes with the suppression of T$_c$ caused by electron doping [11]. By further suppressing T$_c$ by introducing additional impurities in the system, we may have limited the maximum H$_{c2}$ attainable through carbon doping.

4 Conclusions

We have established a method for synthesizing Mg(B$_{1-x}$C$_x$)$_2$ using a mixture of distilled magnesium, boron and the binary compound B$_4$C. Impurities in the starting boron effect T$_c$ and the magnitude of the a-lattice parameter. By tracking $|\Delta a|$ and T$_c$ we were able to show that different boron purities lead to differing T$_c$($|\Delta a|$) manifolds. There appears to be a solubility limit in the carbon content for samples synthesized at 1200 °C and 1 atm near $x\sim 0.07$. Lower purity boron in the starting material results in lower transition temperatures and appears to limit the maximum achievable upper critical field.
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Fig. 1. Powder x-ray diffraction (002) and (110) peaks for pure and nominal Mg(B₁₀₆₅C₀₅)₂ samples made using the 0.995 purity boron as the starting material. The pure sample was reacted using two steps. For the carbon doped sample, the second sintering step shifts the (110) peak position to higher 2θ indicating the incorporation of a higher carbon concentration.
Fig. 2. Normalized magnetization curves for nominal Mg(B\textsubscript{0.95}C\textsubscript{0.05})\textsubscript{2} samples. The second sintering step lowers T\textsubscript{c}, consistent with the incorporation of a higher carbon concentration.
Fig. 3. Normalized powder x-ray pattern for a sample with $x_n=0.05$ synthesized using a one step and a two step reaction. The two step sample clearly contains enhanced amounts of MgB$_4$. 
Fig. 4. (a) Normalized magnetization curves and (b) x-ray (002) and (110) peaks for a sample of $x_n=0.05$ reacted using a two step process. If the second sintering step is performed without any excess Mg to compensate for potential losses, the resultant carbon content within the MgB$_2$ phase is increased.
Fig. 5. (a) Evolution of the (002) and (110) x-ray peaks for Mg(B1−xCx)2 samples with nominal $x_n=0$, 0.0125, 0.025, 0.035, 0.05, 0.075, and 0.20 synthesized using a two step reaction. The shift of the (110) peak relative to that of the un-doped yields inferred carbon concentrations of $x_i=0.01$, 0.034, 0.044, 0.069, 0.067, 0.065. (b) For samples saturating near $x_i=0.07$ the excess carbon precipitates out in the form of MgB$_2$C$_2$ as can be seen by the emergence of the MgB$_2$C$_2$ (042) peak as a function of nominal carbon content.
Fig. 6. Normalized magnetic transitions for the series of \( \text{Mg} (\text{B}_{1-x} \text{C}_x)_2 \) with \( x_{12} = 0.01, 0.034, 0.044, 0.069, 0.067, 0.065 \), synthesized with 0.995 purity B and reacted using a two step process.
Fig. 7. (a) (002) and (110) x-ray peaks for nominal Mg(B_{0.8}C_{0.2})_{2} using B_{4}C as the boron and carbon source and reacted using 1, 2, and 3 step reaction processes. (b) Normalized magnetic transitions for these samples.
Fig. 8. (a) Resistance versus temperature and (b) resistance versus field for a sample with $x_{\text{y2}} = 0.069$. 
Fig. 9. Comparison of upper critical field curves for pellets with carbon doping levels of $x_{i2} = 0.034$ and 0.069 with wires containing $x_i = 0$ and 0.052. The $x_i = 0$ and 0.052 samples were made by reacting Mg vapor with boron filaments, see reference [7].
Fig. 10. Evolution of $T_c$ as a function of $x_i$. CVD wires and powders are from references [12] and [24] respectively. Data on the sample prepared with isotopically enriched $^{11}$B$_4$C is from reference [20].
Fig. 11. Comparison of (002) and (110) x-ray diffraction peaks for pure MgB$_2$ made using different purity boron as the starting material. The 0.995 purity shows a shift in the (110) peak which presumably is not a result of inadvertent carbon doping.
Fig. 12. $H_{c2}(T=0)$ curves for the samples with different purity in the starting boron. CVD wires and plasma spray powders are from references [12] and [24] respectively. $H_{c2}$ data on the highest doping level is from reference [25].