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Optimization of nominal mixing ratio of Mg to B in fabrication of magnesium diboride bulk

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Optimization of Nominal Mixing Ratio of Mg to B in Fabrication of Magnesium Diboride Bulk

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Abstract—In this paper bulk magnesium diboride (MgₓB₂) with x varying from 0.9 to 1.3 was prepared by solid state reaction. The Mg:B mixing ratio for ideal MgB₂ is 1:2. The samples were sintered at 800°C for 60 h. Quantitative X-ray diffraction (XRD) analysis was performed to obtain the lattice parameters, the microstrain, and the weight fraction of impurities using the Rietveld refinement method. It has been found that the fraction of pure MgB₂ phase increases from x = 0.9 to x = 1.1, and then decreases with further increases in x. Mg₁₋₁,B₂ exhibits the highest critical current density, Jc, over other samples in both low fields and high fields. A direct correlation between Jc and connectivity indicates that better connectivity, caused by smaller amounts of impurities, results in the best Jc in Mg₁₋₁,B₂.

Index Terms—Connectivity, MgB₂, nominal mixing ratio, superconductivity.

I. INTRODUCTION

MgB₂ is a promising metallic superconductor operating at relatively high temperatures around 20 K [1]. MgB₂ exhibits several prominent characteristics, including a high transition temperature, a simple crystal structure, abundance of the raw materials in nature, and the absence of weak intergranular links. However, the weak flux pinning, low critical current density (Jc) in high fields, and low irreversibility field (Hirr) are retarding its application. Numerous efforts have been focused on the improvement of Jc by chemical doping [2], [3], ball-milling methods [4], [5], thermo-mechanical processing methods [6]–[8], and proton irradiation [9].

It has been found that the stoichiometry of MgB₂ significantly affects the superconducting properties. Unfortunately, discrepancies on this topic still exist. Jiang et al. [10] reported that slightly Mg-deficient samples showed higher Jc in high fields, whereas samples with stoichiometric Mg or a slight excess of Mg exhibited better Jc in low fields. The reason for higher Jc in high fields was attributed to the enhanced grain boundary pinning caused by the smaller grain size. Perner et al. [11] found that the best critical temperature (Tc) and Jc were obtained for an Mg surplus of 5 wt%. Chen et al. [12] reported that nominally Mg-deficient samples had enhanced in-field Jc values over samples prepared in an Mg excess environment. They attributed this to the increased structural disorder. In this paper, we systematically investigated the effects of the nominal mixing ratio of Mg to B, which was varied from 0.9:2 to 1.3:2, on the superconducting properties of MgₓB₂. The Mg:B mixing ratio for ideal MgB₂ is 1:2. A detailed analysis of the fraction of each phase, the lattice parameters, microstrain, Tc, the upper critical field (Hc₂), Jc, and connectivity has been conducted. It was found that the sample with x = 1.1 exhibited the highest Jc in all fields at 5 K and 20 K. A clear correlation between Jc and connectivity indicates that the good connectivity in the sample with 10% Mg excess caused the Jc enhancement in both low fields and high fields.

II. EXPERIMENTAL

MgₓB₂ samples with x = 0.9, 1, 1.1, 1.2, and 1.3 were prepared by solid state reaction. Mg powder (1–11 μm) and amorphous boron powder (99%) were used as the starting materials. The powders were carefully mixed by grinding in a mortar and pressed into pellets 13 mm in diameter and about 2.5 mm thick. The pellets were sealed into Fe tubes. The sealed tubes were then heated in a tube furnace under pure Ar gas and sintered at 800°C for 60 h prior to cooling to room temperature.

The obtained MgₓB₂ samples were examined by X-ray diffraction (XRD) in a Philips PW1730 Model diffractometer using Cu Kα radiation (λ = 1.5418 Å). The XRD patterns were collected over a 2θ range from 20° to 80° with a step size of 0.02°. Lattice parameter calculations and quantitative phase analysis were carried out based on the XRD patterns. Magnetic measurements of the samples were conducted in a commercial Quantum Design Physical Properties Measurement System (PPMS) after they have been polished into a cuboid shape for measurements. Their dimensions were accurately measured with a digital micrometer. The DC magnetic response was obtained in an applied low field of 1 Oe using the conventional zero-field-cooled (ZFC) and field-cooled (FC) procedures. Magnetic hysteresis loops were measured at temperatures of 5 K and 20 K. The critical current density was calculated from the magnetization hysteresis loops, based on the dimensions of the samples. The resistivity was measured as a function of temperature and magnetic field, using a four probe resistance technique.

III. RESULTS AND DISCUSSION

Fig. 1 shows the powder XRD patterns of MgₓB₂ samples with x = 0.9, 1, 1.1, 1.2, and 1.3. All the major peaks of the

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MgB$_2$ hexagonal structure (space group P6/mmm) can be identified, indicating that the samples mainly consisted of the desired MgB$_2$ phase. Besides MgB$_2$, the impurity MgO existed in all the samples. Two strong peaks of the MgO phase are located at $2\theta \approx 42.90^\circ$ and $2\theta \approx 62.28^\circ$. Another two weaker peaks at $2\theta \approx 36.80^\circ$ and $2\theta \approx 78.54^\circ$ can also be observed in the XRD patterns. MgO impurities could be formed by reactions during the sintering process. The reacting oxygen could be introduced from the air trapped in the tubes and also from oxygen in the starting boron powders. For the samples with $x < 1.1$, MgB$_4$ was detected. MgB$_4$ exists due to a deficiency of magnesium, which is caused by evaporation of the magnesium and formation of MgO. At $x \approx 1.1$, MgB$_4$ disappears, and only MgO impurities can be observed. When $x$ further increases to 1.2, magnesium metal becomes excessive. Therefore, two major peaks of magnesium metal are displayed in the XRD patterns of Mg$_{1.2}$B$_2$ and Mg$_{1.3}$B$_2$ at $2\theta \approx 36.62^\circ$ and $2\theta \approx 32.12^\circ$.

Rietveld refinement was performed to analyze the XRD measurements. The refinable parameters include the weight fraction of each phase, the lattice parameters of MgB$_2$, and the percentage of microstrain. A measure of similarity ($R_{wp}$) between the measured diffraction patterns and the simulated diffraction patterns is shown in Table I. A low $R_{wp}$ indicates good agreement between the measured and simulated data. All the $R_{wp}$ values are below 7.5%. This indicates that the calculated results are acceptable. The calculated weight fraction of each phase in the samples is also listed in Table I. It was found that the weight fraction of pure MgB$_2$ phase increased from $x = 0.9$ to $x = 1.1$, and then decreased. There are large differences in the weight fraction of MgB$_2$ phase in the samples, varying from 69.03% to 90.03%. The weight fraction of MgO increases with $x$. A large amount of MgB$_3$ phase exists in Mg$_{0.9}$B$_2$ and Mg$_{0.9}$B$_2$. Its weight fraction increases with decreasing $x$. It seems that the existence of MgB$_3$ significantly reduces the weight fraction of MgB$_2$ phase. A small amount of Mg appears in the samples with sufficient Mg precursor powder (Mg$_{0.1}$B$_2$ and Mg$_{0.1}$B$_2$). Its fraction increases with $x$.

The calculated in-plane lattice constant ($a$) in the samples is nearly the same. The inter-plane lattice constant ($c$) decreases from 3.526 Å to 3.519 Å with increasing $x$. The lattice constant $c$ of Mg$_{0.9}$B$_2$ is larger than the value for the ideal MgB$_2$ structure ($c = 3.521$ Å). This indicates that a large amount of vacancies exist in the sample. This can be attributed to the nominal deficiency of magnesium in Mg$_{0.9}$B$_2$ and the formation of MgO. For the sample with stoichiometric Mg ($x = 1$), the Mg deficiency and the vacancies still exist, due to the formation of MgO. As the nominal ratio of Mg to B ($x:2$) increases, the nominal or real deficiency of Mg decreases. Therefore, the vacancies in the samples are reduced, resulting in a decreased $c$, as depicted in Table I. In the Mg$_{1.3}$B$_2$ sample, the magnesium deficiency disappears, and boron becomes more than sufficient. The redundant boron atoms may diffuse into the MgB$_2$ lattice as interstitial atoms, leading to a smaller lattice parameter $c$ than the ideal value ($c = 3.521$ Å).

Table I also shows that microstrain varies from 0.167% to 0.229%. Mg$_{1.3}$B$_2$ has the largest microstrain, while MgB$_3$ exhibits the smallest one. Microstrain does not monotonically vary with the nominal ratio of Mg to B. The reason can be attributed to the effect of the MgB$_3$ and Mg impurities. The existence of the impurity can change microstrain. MgB$_3$ appears in Mg$_{0.9}$B$_2$ and Mg$_{1.2}$B$_2$ and its amount decreases with $x$, while the metal Mg phase exists in Mg$_{1.2}$B$_2$ and Mg$_{1.3}$B$_2$ and its amount increases with $x$. The variation of amount of these impurities produces a complicated relationship between microstrain and the nominal ratio of Mg to B.

Fig. 2 shows a plot of the magnetic susceptibility against the temperature in an applied field of $H = 1$ Oe for zero field cooled samples. The magnetic susceptibility for the field cooled condition is not displayed in the figure, since the values are very close.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$R_{wp}$ (%)</th>
<th>Weight fraction (%)</th>
<th>Lattice Parameters (Å)</th>
<th>Microstrain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$_{1.0}$B$_2$</td>
<td>7.48</td>
<td>69.03, 7.06, 23.91</td>
<td>3.085, 3.526</td>
<td>0.201</td>
</tr>
<tr>
<td>MgB$_2$</td>
<td>5.87</td>
<td>73.2, 7.53, 19.27</td>
<td>3.084, 3.525</td>
<td>0.167</td>
</tr>
<tr>
<td>Mg$_{1.1}$B$_2$</td>
<td>6.05</td>
<td>90.03, 9.97</td>
<td>3.084, 3.525</td>
<td>0.216</td>
</tr>
<tr>
<td>Mg$_{1.2}$B$_2$</td>
<td>6.38</td>
<td>88.73, 10.4</td>
<td>0.87, 3.085, 3.523</td>
<td>0.185</td>
</tr>
<tr>
<td>Mg$_{1.3}$B$_2$</td>
<td>6.202</td>
<td>85.07, 12.67</td>
<td>2.25, 3.084, 3.519</td>
<td>0.229</td>
</tr>
</tbody>
</table>

Table I

Refined Parameters in Mg$_x$B$_2$
This demonstrates that the flux pinning force in all the samples is quite large. The critical temperature ($T_c$) is defined as the temperature corresponding to the onset of diamagnetism, and the transition width ($\Delta T_c$) is defined as the temperature variation between 10% and 90% of the full drop in the magnetic susceptibility. From Table II it can be seen that $T_c$ is similar for all the samples within a range of 0.5 K, which is consistent with the observations of Chen et al. [12]. $T_c$ slightly decreases with $x$. It also linearly decreases with the lattice parameter $c$. A decrease in the lattice parameters reduces the electronic density of states (DOS) at the Fermi level and hardens the optical phonons [13]. The reduction in the DOS and the hardening of the $F_{2g}$ phonons depresses $T_c$. $\Delta T_c$ in all the samples is sharp, with a width of $\sim 1$ K as shown in Fig. 2. This indicates that the $\text{MgB}_2$ phase is quite homogeneous.

The resistivity ($\rho$) results are shown in Fig. 3. It can be observed that the resistivities in the samples with $x \geq 1.1$ are close to each other. The resistivity increases as $x$ decreases from 1.1 to 0.9. The resistivities at 40 K and 300 K ($\rho_{40\text{K}}$ and $\rho_{300\text{K}}$) were collected from Fig. 3 and are listed in Table II. $\text{MgB}_2$ has the smallest $\rho_{40\text{K}}$, while $\rho_{300\text{K}}$ in $\text{MgB}_2$ is smallest. All $\rho_{40\text{K}}$ are higher than for single crystal (5.3 $\mu\Omega\text{cm}$, [14]) and for dense filaments made by chemical vapor deposition (CVD) (7.3 $\mu\Omega\text{cm}$, [15]). The reason can be attributed to poor connectivity in the studied samples. The XRD traces in Fig. 1 show the presence of a large amount of MgO in the samples. MgO is mainly present in the grain boundaries as an insulator, which reduces the effective cross-sectional area of the samples and then increases the resistivity. The impurity $\text{MgB}_4$ also increases the resistivity in $\text{Mg}_{0.3}\text{B}_2$ and $\text{MgB}_2$. The presence of Mg metal can reduce the resistivity, since Mg is a good conductor. However, the influence of Mg is not significant because its amount is quite small. The effective cross-sectional area ($A_F$) can be estimated from the equation, $A_F = \frac{\Delta \rho_{\text{ideal}}}{\rho_{300\text{K}} - \rho_{40\text{K}}}$. This indicates that the flux pinning force in all the samples is sharp in resistivity from 300 K to 40 K for a fully connected sample. It was set to be 7.3 $\mu\Omega\text{cm}$ according to [17]. The calculated $A_F$ is displayed in Table II. $A_F$ varies from 0.13 to 0.252, indicating poor connection in the samples. It can be noted from Tables I and II that $A_F$ is related to the weight fraction of the $\text{MgB}_2$ phase. This reveals that the poor connectivity is mainly caused by the impurities.

The critical current density was calculated from the measured magnetization hysteresis loops, with the calculation based on the Bean model. Critical current densities at 5 K and 20 K are shown in Fig. 4. $J_c$ in the flux jumping region is not shown in the figure. It is clear that $\text{MgB}_2$ has the maximum $J_c$ for all the fields at both 5 K and 20 K. This means that 1.1:2 is the optimum nominal mixing ratio of Mg to B under current processing conditions. The $\text{Mg}_{0.3}\text{B}_2$ sample has the lowest $J_c$. 

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**Table II: Properties of $\text{Mg}_x\text{B}_2$**

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_c$ (K)</th>
<th>$J_c$ at 0T and 20K (Acm$^{-2}$)</th>
<th>$J_c$ at 4.6T and 20K (Acm$^{-2}$)</th>
<th>$\rho_{40\text{K}}$ (\mu\Omega cm)</th>
<th>$\rho_{300\text{K}}$ (\mu\Omega cm)</th>
<th>$A_F$</th>
<th>$H_{c2}$ at 20K (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$_{0.1}$B$_2$</td>
<td>37.88</td>
<td>170399</td>
<td>137</td>
<td>50.38</td>
<td>106.51</td>
<td>0.130</td>
<td>9.24</td>
</tr>
<tr>
<td>Mg$_{0.2}$B$_2$</td>
<td>37.62</td>
<td>228777</td>
<td>147</td>
<td>31.51</td>
<td>70.42</td>
<td>0.188</td>
<td>8.69</td>
</tr>
<tr>
<td>Mg$_{0.3}$B$_2$</td>
<td>37.55</td>
<td>397933</td>
<td>1042</td>
<td>22.48</td>
<td>51.44</td>
<td>0.252</td>
<td>9.4</td>
</tr>
<tr>
<td>Mg$_{0.4}$B$_2$</td>
<td>37.53</td>
<td>374204</td>
<td>226</td>
<td>21.49</td>
<td>53.79</td>
<td>0.226</td>
<td>9.18</td>
</tr>
<tr>
<td>Mg$_{0.5}$B$_2$</td>
<td>37.39</td>
<td>366490</td>
<td>157</td>
<td>23.57</td>
<td>57.87</td>
<td>0.213</td>
<td>9.71</td>
</tr>
</tbody>
</table>

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"Fig. 2. Magnetic susceptibility plotted against temperature."

"Fig. 3. Resistivity versus temperature for the samples."
As x increases from 0.9 to 1.1, J_c increases. J_c decreases when x increases from 1.1 to 1.3.

The J_c values at zero field and 20 K (J_c(20 K)) are listed in Table II. The correlation between J_c(20 K) and A_F is shown in Fig. 5. The solid line represents the trend, as a good linear relationship can be observed. This indicates that the self-field J_c is mainly influenced by the connectivity. J_c at high field (4.6 T) and 20 K is also listed in Table II. J_c at high fields is mainly determined by the H_c2 and the connectivity [13]. H_c2 at 20 K, measured at 90% of the normal state resistivity, is shown in Table II. H_c2 at 20 K as a function of microstrain is presented in Fig. 6. It is clear that H_c2 linearly increases with microstrain. H_c2 is determined by the disorder in MgxB_2, whereas microstrain is a measure of the disorder. A lower microstrain is suggestive of a larger mean free path (l) of the superconducting electrons. This will increase the coherence length (ξ). According to H_c2 = φ_0/(2πlμ_0ξ^2), where φ_0 is the superconducting flux quantum and μ_0 is the magnetic permeability, H_c2 will decrease as ξ increases. It was not possible to find a monotonic relationship between H_c2 and J_c at high field (4.6 T) and 20 K from the results listed in Table II. This implies that another factor besides H_c2 may play a more important role in J_c at high fields. Comparing the values of J_c at 4.6 T and 20 K with the connectivity (A_F) shows that J_c increases with A_F. Mg_{1.1}B_2 has the largest A_F and highest J_c. Therefore, the connectivity is very likely to be the major reason for the J_c difference at high fields in the studied samples.

IV. CONCLUSION

Mg_xB_2 samples with x = 0.9, 1.1, 1.2, and 1.3 were prepared by solid state reaction. Quantitative X-ray diffraction (XRD) analysis was performed to obtain the lattice constants, the microstrain, and the weight fraction of impurities using the Rietveld method. It has been found that the fraction of pure MgB_2 phase increases from x = 0.9 to x = 1.1, and then decreases with further increases in x. The critical temperature (T_c) increases with the lattice parameter c. In Mg_{1.3}B_2 samples, J_c increases with x to the maximum value at x = 1.1 and then decreases. The higher J_c at x = 1.1 is attributed to the better connectivity caused by smaller amounts of impurities.

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