Improvement of Critical Current Density and Upper Critical Field in MgB₂ using Carbohydrate

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Abstract— We evaluated the doping effects of carbohydrate (malic acid, C₄H₆O₅) from 0wt% to 30wt% of total MgB₂, on the phase, lattice parameters, critical temperature (T_c), resistivity (ρ), and upper critical field (H_{c2}) of MgB₂ superconductor. The lattice parameters calculated show a large decrease in the a-axis for MgB₂+C₄H₆O₅ samples, but no change in the c-axis. This is an indication of the carbon (C) substitution into B coming from C₄H₆O₅, resulting in enhancement of ρ, J_c, and H_{c2}. Specifically, the J_c value of 2.5 x 10⁸ Acm⁻² at 5 K and 8 T for the MgB₂+30wt% C₄H₆O₅ sample is higher than that of the un-doped MgB₂ by a factor of 21. In addition, ρ value for all the MgB₂+C₄H₆O₅ samples ranged from 80 µΩcm to 90 µΩcm at 40 K, which is higher than for un-doped MgB₂. The increased ρ indicates increased impurity scattering due to C, resulting in enhanced H_{c2}.

Index Terms— carbohydrate, malic acid, MgB₂, upper critical field

I. INTRODUCTION

THE discovery of the superconductivity of MgB₂ at 39 K could offer the promise of important large-scale applications at around 20 K [1]. A significant enhancement in J_c of MgB₂ has been achieved through chemical doping with carbon (C) containing compounds, such as SiC, C, B₄C, and CNT [2-5]. In particular, C can enter the MgB₂ structure by the substitution for B to increase impurity scattering into the two-band MgB₂ and hence significantly increase J_c and H_{c2}. However, the doping effect for MgB₂ superconductor has been limited by the agglomeration of nano-sized dopants and poor reactivity between boron (B) and C. Un-reacted C remain in the MgB₂ matrix and react with Mg or B powders, resulting in the formation of impurity phases. To overcome these properties, it is further necessary to study the homogeneity of mixing as well as the activity of reaction between B and C materials. The various methods have been studied by many groups. Ribeiro et al. reported that B₄C was considered to be one of the more reactive C containing compounds because free C was liberated from B₄C [6]. However, using B₄C compound was needed higher sintering temperature up to 1200°C as well as longer sintering time. Dou et al. studied the effect of SiC doping on the MgB₂ superconductor [7]. Even though SiC material was much more effective at enhancing the J_c at a low sintering temperature (~650°C), there were agglomerations of nano-particles in the MgB₂ matrix.

In this study, therefore, we used malic acid (C₄H₆O₅) as a representative carbohydrate dopant. Because of the high reactivity of freshly formed C, the C substitution for B can take place at the same temperature as the formation temperature of MgB₂. Carbohydrates can be dissolved in a solvent (~150°C) so that the solution can form a slurry with B powder. After evaporating the solvent the carbohydrate forms a coating on the B powder surfaces, giving a highly uniform mixture. For these reasons, the doping effects of carbohydrate material on the MgB₂ superconductor were evaluated. We fabricated MgB₂ superconductor with C₄H₆O₅ included. The phase, lattice parameters, critical temperature (T_c), resistivity (ρ), J_c, and H_{c2} are presented in comparison with the un-doped reference MgB₂.

II. EXPERIMENTAL PROCEDURE

MgB₂ pellets were prepared by an in-situ reaction process with addition of malic acid, C₄H₆O₅. The amount of C₄H₆O₅ (99%), from 0wt% to 30wt% of total MgB₂, was mixed with an appropriate amount of B (99%) in toluene (C₆H₆, 99.5%). This slurry was dried in vacuum so that the B powder was coated by the C coming from C₄H₆O₅. Since decomposition temperature of C₄H₆O₅ was at around 150°C. This uniform composite was then mixed with an appropriate amount of Mg (99%) powder. These mixed powders were ground, pressed and then sintered at 900°C for 30 min under high purity argon gas. The heating rate was 5°C/min. All samples were characterized by X-ray diffraction (XRD). The crystal structure was refined with the aid of the program FullProf. T_c was defined as the onset temperature at which diamagnetic properties were observed. The magnetization was measured at 5 and 20 K using a Physical Property Measurement System (PPMS, Quantum Design) in a time-varying magnetic field with sweep rate 50 Oe/s and amplitude 8.5 T. Since there is a large sample size effect on the magnetic J_c for MgB₂ all the samples for measurement were made to the same size (1 x 2.2 x 3.3 mm³) for comparison [5]. The magnetic J_c was derived from the width of the magnetization loop using Bean’s model. In addition, H_{c2} was
defined as $H_c^2=0.9R(T_c)$ from the resistance ($R$) versus temperature ($T$) curve.

### III. RESULTS AND DISCUSSIONS

Figure 1 shows the XRD result for un-doped MgB$_2$ and MgB$_2$ + C$_4$H$_6$O$_5$ samples. The XRD measurements were performed on the ground MgB$_2$ cores. It was observed that the four different kinds of samples seemed to be well developed MgB$_2$ with a small amount of MgO. XRD patterns of the MgB$_2$ + C$_4$H$_6$O$_5$ sample are almost independent of the sintering temperature. For the MgB$_2$ + 30wt% C$_4$H$_6$O$_5$ sample, however, the relative amount of MgO was slightly larger than for the lightly doped samples. From the XRD results, the full width at half maximum (FWHM) of the (110) and (002) peaks for un-doped and MgB$_2$ + C$_4$H$_6$O$_5$ samples were also evaluated. For example, the FWHMs of the (110) peaks for the un-doped, 10wt%, 20wt%, and 30wt% C$_4$H$_6$O$_5$ samples were calculated to be 0.445°, 0.500°, 0.550°, and 0.535°, respectively, while the corresponding values for the (002) peak were 0.400°, 0.445°, 0.470°, and 0.395°. That is, as the doping level increased to 20wt%, FWHM value linearly increased for both peaks. This significant broadening for the MgB$_2$ + C$_4$H$_6$O$_5$ samples can be explained by lattice distortion due to C substitution from C$_4$H$_6$O$_5$, indicating the degradation of crystallinity of the MgB$_2$ [8]. As the doping level further increased to 30wt%, however, the FWHM value slightly decreased. This observation is related to the improvement of crystallinity.

For further analysis, we calculated the lattice parameters of the $a$- and $c$-axes from the (110) and (002) peaks, respectively, as shown in Figure 2. It was observed that the $a$-axis parameter changed from 3.0835(5) Å to 3.0731(9) Å as the doping level increased to 30wt%. This is attributed to the actual C substitution for B sites. The shrinkage of the $a$-axis occurred due to the difference in atomic size between B and C ions after substitution. On the other hand, the $c$-axis did not change, suggesting that C doping does not affect the $c$-axis. The $c$-axis parameter was in the range of 3.5214(7) Å to 3.5268(3) Å. As a result, C coming from C$_4$H$_6$O$_5$ can be used as a C source, just like SiC, C, B$_4$C and CNT. It is to be noted that the $a$-axis values are almost saturated for the 10wt%, 20wt%, and 30wt% C$_4$H$_6$O$_5$ samples. From the Avdeev et al. results, we also estimated the actual amount of C substitution in our MgB$_2$ + C$_4$H$_6$O$_5$ samples [9]. The value was calculated to be $x \approx 0.038$ to 0.046 in the composition of MgB$_2$$_{1-x}$C$_x$. It is evident that the amount of C substitution for B is much less than the nominal composition. However, even though the actual C levels for C$_4$H$_6$O$_5$ were 1.9at% to 2.3at% of B, the amount of actual C substitution was much higher for other C doped MgB$_2$ sample. This is attributed to the high reactivity of the freshly formed C.

Figure 3 shows the $T_c$ of all samples sintered at 900°C for 30 min. The calculated values were 37.6 K, 35.8 K, 35.7 K, and 35.8 K, respectively. Specifically, the $T_c$ behavior of the MgB$_2$ + 10wt% C$_4$H$_6$O$_5$ sample had a two-step behavior near the onset temperature. This is probably related to inhomogeneity of the mixed powder between B and C. In this experiment, using toluene solution is believed to be much more effective for

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**Fig. 1.** The x-ray diffraction patterns for un-doped MgB$_2$ and MgB$_2$ + C$_4$H$_6$O$_5$ samples with different compositions.

**Fig. 2.** Lattice parameters $a$- and $c$-axis as a function of the C$_4$H$_6$O$_5$ contents.

**Fig. 3.** Critical temperature as a function of the C$_4$H$_6$O$_5$ contents.
preparing homogeneous powder, since carbohydrate is easy to dissolve in toluene. After decomposition of the carbohydrate, C remaining C can from a coating on the surface of the B powder, resulting in homogeneous mixing. For future work, we need further systematical study on the use of solution methods. In addition, we observed that $T_c$ broadening occurred for the MgB$_2$ + C$_6$H$_{12}$O$_6$ samples. This could be associated with degradation of crystallinity due to C substitution. This result is consistent with the results from the FWHM and lattice parameter.

Figure 4 shows the magnetic field dependence of $J_c$ in all samples at 20 K and 5 K. It should be noted that $J_c$ values in high field were increased by more than an order of magnitude. For example, the $J_c$ value of $2.5 \times 10^4$ Acm$^{-2}$ at 5 K and 8 T for the MgB$_2$ + 30wt% C$_6$H$_{12}$O$_6$ sample is higher than that of the un-doped MgB$_2$ by a factor of 21. In addition, there was no $J_c$ degradation in self-field for the MgB$_2$ + 30wt% C$_6$H$_{12}$O$_6$ sample. The estimated $J_c$ value was $4.0 \times 10^4$ Acm$^{-2}$ at 20 K and self-field.

The temperature dependence of $H_{c2}$ for all samples is shown in Figure 5. Significantly enhanced $H_{c2}$ for MgB$_2$ + C$_6$H$_{12}$O$_6$ samples was observed, suggesting that C substitution into B sites results in an enhancement in $H_{c2}$. The $\rho_s$ for the un-doped and MgB$_2$ + C$_6$H$_{12}$O$_6$ samples are 34 $\mu$Ω·cm and 80 $\mu$Ω·cm to 90 $\mu$Ω·cm at 40 K, respectively. The increased $\rho$ for MgB$_2$ + C$_6$H$_{12}$O$_6$ samples indicates the increased impurity scattering as a result of C substitution into B sites. It is to be noted that RRR values from the formula $\rho(300K)/\rho(40K)$ slightly increased as the doping level increased. These values were 2.13, 1.62, 2.34, and 2.23 for corresponding compositions. These relatively high values of RRR indicate that the samples are of good quality, even the 20wt% and 30wt% doping samples.

As a result, the significant advantages of carbohydrate are: (1) the carbohydrates in the mixture melt at lower temperatures and decompose at temperatures below the formation temperature of MgB$_2$, hence producing highly reactive and fresh C on the atomic scale: and (2) as carbohydrates consist of a large range of materials, this work will have significant implications for further improvement of the performance properties of MgB$_2$, as well as many other C-based compounds and composites.

IV. CONCLUSIONS

We evaluated the doping effects of malic acid, C$_6$H$_{12}$O$_6$, from 0wt% to 30wt% of total MgB$_2$, on the phase, lattice parameters, FWHM, $T_c$, $\rho_s$, $J_c$, and $H_{c2}$ of MgB$_2$ superconductor. We observed that all samples sintered at 900°C seemed to be well-developed MgB$_2$ with small amounts of MgO. However, the FWHMs related to the (110) and (002) peaks were larger for MgB$_2$ + C$_6$H$_{12}$O$_6$ samples than for un-doped MgB$_2$. This indicates that lattice distortion had occurred due to the C coming from C$_6$H$_{12}$O$_6$. In addition, the $a$-axis parameter changed from 3.0835(5) Å to 3.0731(9) Å as the doping level increased to 30wt%. The actual C substitutions were calculated to be $x \sim 0.038$ to 0.046 in the composition of MgB$_2$C$_x$.

Specifically, MgB$_2$ + C$_6$H$_{12}$O$_6$ samples exhibited excellent $J_c$ and $H_{c2}$. This result indicates that strong flux pinning was enhanced by C coming from C$_6$H$_{12}$O$_6$. The carbohydrate is promising C source for MgB$_2$ superconductor with excellent $J_c$ and $H_{c2}$.

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