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# Carbohydrate doping to enhance electromagnetic properties of MgB<sub>2</sub> superconductors

Jung Ho Kim

*University of Wollongong, jhk@uow.edu.au*

Sihai Zhou

*University of Wollongong, sihai@uow.edu.au*

Md S. Hossain

*University of Wollongong, shahriar@uow.edu.au*

Alexey V. Pan

*University of Wollongong, pan@uow.edu.au*

S X. Dou

*University of Wollongong, shi@uow.edu.au*

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# Carbohydrate doping to enhance electromagnetic properties of MgB<sub>2</sub> superconductors

## Abstract

The effect of carbohydrate doping on lattice parameters, microstructure,  $T_c$ ,  $J_c$ ,  $H_{irr}$ , and  $H_{c2}$  of MgB<sub>2</sub> has been studied. In this work the authors used malic acid as an example of carbohydrates as an additive to MgB<sub>2</sub>. The advantages of carbohydrate doping include homogeneous mixing of precursor powders, avoidance of expansive nanoadditives, production of highly reactive C, and significant enhancement in  $J_c$ ,  $H_{irr}$ , and  $H_{c2}$  of MgB<sub>2</sub>, compared to undoped samples. The  $J_c$  for MgB<sub>2</sub>+30 wt% C<sub>4</sub>H<sub>6</sub>O<sub>5</sub> sample was increased by a factor of 21 at 5 K and 8 T without degradation of self-field  $J_c$ .

## Keywords

Carbohydrate, doping, enhance, electromagnetic, properties, MgB<sub>2</sub>, superconductors

## Disciplines

Engineering | Physical Sciences and Mathematics

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## Carbohydrate doping to enhance electromagnetic properties of MgB<sub>2</sub> superconductors

J. H. Kim, S. Zhou, M. S. A. Hossain, A. V. Pan, and S. X. Dou<sup>a)</sup>

*Institute for Superconducting and Electronic Materials, University of Wollongong, Northfields Ave., Wollongong, New South Wales 2522, Australia*

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The effect of carbohydrate doping on lattice parameters, microstructure,  $T_c$ ,  $J_c$ ,  $H_{irr}$ , and  $H_{c2}$  of MgB<sub>2</sub> has been studied. In this work the authors used malic acid as an example of carbohydrates as an additive to MgB<sub>2</sub>. The advantages of carbohydrate doping include homogeneous mixing of precursor powders, avoidance of expansive nanoadditives, production of highly reactive C, and significant enhancement in  $J_c$ ,  $H_{irr}$ , and  $H_{c2}$  of MgB<sub>2</sub>, compared to undoped samples. The  $J_c$  for MgB<sub>2</sub>+30 wt % C<sub>4</sub>H<sub>6</sub>O<sub>5</sub> sample was increased by a factor of 21 at 5 K and 8 T without degradation of self-field  $J_c$ . © 2006 American Institute of Physics. [DOI: 10.1063/1.2358947]

With the relatively high critical temperature ( $T_c$ ) of 39 K (Ref. 1) and the high critical current density ( $J_c$ ) of  $>10^5$  cm<sup>-2</sup> in moderate fields, magnesium diboride (MgB<sub>2</sub>) superconductors could offer the promise of important large-scale applications to be operated at 20 K. A significant enhancement in the electromagnetic properties of MgB<sub>2</sub> has been achieved through doping with various forms of carbon (C).<sup>2-6</sup> To take advantage of its  $T_c$  of 39 K, enhancements of both the upper critical field ( $H_{c2}$ ) and  $J_c$  are essential. Attempts to accomplish this have invoked the introduction of numerous techniques including chemical doping,<sup>2-6</sup> irradiation,<sup>7</sup> and various thermomechanical processing techniques.<sup>8,9</sup> Chemical doping is a simple and readily scalable technique. Since MgB<sub>2</sub> has a relatively large coherence length and small anisotropy, the fluxoids to be pinned are stringlike and amenable to pinning by inclusions and precipitates in the grains.

Among the numerous forms of C-containing dopants, SiC doping has achieved a record high in-field  $J_c(B)$ ,  $H_{c2}$ , and irreversibility ( $H_{irr}$ ) in MgB<sub>2</sub>.<sup>2</sup> These record high properties have been confirmed and reproduced by many groups,<sup>2,5,10,11</sup> and the performance records remain unbroken up to now. However, the best high-field  $J_c$  values achieved in the SiC doped MgB<sub>2</sub> wires were compromised by the reduction in self-field and low-field  $J_c$ . Although nanosize precursor particles were chosen for the doping process it is a great challenge to achieve homogeneous distribution of a small amount of nanodopants within the matrix materials through solid state mixing. There are always agglomerates of nanoadditives in the precursors. For various forms of C doping, the substitution of C for boron (B) cannot be achieved at the same temperatures as that of the MgB<sub>2</sub> formation reaction due to their poor reactivity.

In order to overcome these problems we proposed to use a carbohydrate such as DL-malic acid (C<sub>4</sub>H<sub>6</sub>O<sub>5</sub>) as the dopant. The significant advantages of carbohydrate are as follows. (1) Carbohydrates can be dissolved in a solvent 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. (2) The

carbohydrates in the mixture melt at lower temperatures and decompose at temperatures below the formation temperature of MgB<sub>2</sub>, hence producing highly reactive and fresh C on the atomic scale, as well as a reducing reagent, carbon monoxide, which may convert boron oxide to B, reducing the impurities in B powder. (3) Because of the high reactivity of the freshly formed C, the C substitution for B can take place at the same temperature as the formation temperature of MgB<sub>2</sub>. The simultaneous dual reactions promote C substitution for B in the lattice and the inclusion of excess C within the grains, resulting in the enhancement of  $J_c$ ,  $H_{irr}$ , and  $H_{c2}$ .

In this study, therefore, we used malic acid as a representative of carbohydrate dopant. We fabricated MgB<sub>2</sub>+C<sub>4</sub>H<sub>6</sub>O<sub>5</sub> samples with different addition levels. The lattice parameters  $T_c$ ,  $J_c$ ,  $H_{irr}$ ,  $H_{c2}$ , and microstructures are presented in comparison with the undoped reference MgB<sub>2</sub>. MgB<sub>2</sub> pellets were prepared by an *in situ* reaction process with the addition of C<sub>4</sub>H<sub>6</sub>O<sub>5</sub>. The selected amount of C<sub>4</sub>H<sub>6</sub>O<sub>5</sub> (99%), from 0 to 30 wt % of total MgB<sub>2</sub> was mixed with an appropriate amount of B (99%) powder in toluene (C<sub>7</sub>H<sub>8</sub>, 99.5%). This slurry was dried in vacuum so that the B powder particles were coated by the C coming from C<sub>4</sub>H<sub>6</sub>O<sub>5</sub>. Since the decomposition temperature of C<sub>4</sub>H<sub>6</sub>O<sub>5</sub> 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 argon gas. All samples were characterized by x-ray diffraction (XRD), field emission gun-scanning electron microscopy (FEG-SEM),  $J_c$ ,  $T_c$ ,  $H_{irr}$ , and  $H_{c2}$ .<sup>3</sup> The lattice parameters were obtained from Rietveld refinement.

Table I shows the measured data for the undoped MgB<sub>2</sub> and MgB<sub>2</sub>+C<sub>4</sub>H<sub>6</sub>O<sub>5</sub> samples with different addition levels. The lattice parameters calculated from XRD show a large decrease in the *a*-axis parameter with 10 wt % C<sub>4</sub>H<sub>6</sub>O<sub>5</sub> and a small further drop in *a* with increasing C<sub>4</sub>H<sub>6</sub>O<sub>5</sub> addition level, but no change in the *c*-axis parameter. This is an indication of the C substitution for B. The actual C substitution level can be estimated from the *a*-axis change.<sup>12</sup> It should be noted that the net C percentage addition is only 36% of the C<sub>4</sub>H<sub>6</sub>O<sub>5</sub> addition. The actual C substitution levels of 1.9–2.3 at % of B at three doping levels are clearly higher than those with other forms of C dopants, which is attributable to the high reactivity of fresh C released from the de-

<sup>a)</sup> Author to whom correspondence should be addressed; electronic mail: shi\_dou@uow.edu.au

TABLE I. Measured data for undoped  $\text{MgB}_2$  and  $\text{MgB}_2+\text{C}_4\text{H}_6\text{O}_5$  samples with different addition levels.  $H_{\text{irr}}^*$  was calculated from the standard criterion of  $J_c$  ( $100 \text{ A cm}^{-2}$ ).

Malic acid ( $\text{C}_4\text{H}_6\text{O}_5$ ) amount (wt %)	Lattice parameters		Actual C (x) in $\text{MgB}_{2-x}\text{C}_x^a$	$T_c$ (K)	$\rho_{40 \text{ K}}$ ( $\mu\Omega \text{ cm}$ )	$\rho_{300 \text{ K}}$ ( $\mu\Omega \text{ cm}$ )	$H_{\text{irr}}^*$ (T) (20 K)	$J_c$ ( $\text{A cm}^{-2}$ )	
	$a$ ( $\text{\AA}$ )	$c$ ( $\text{\AA}$ )						Self-field (20 K)	8 T (5 K)
0	3.0835(5)	3.5217(5)		37.6	34.5	73.5	5.4	$3.9 \times 10^5$	$0.1 \times 10^4$
10	3.0751(6)	3.5268(3)	0.0380	35.8	90.2	146.5	6.7	$3.5 \times 10^5$	$2.3 \times 10^4$
20	3.0746(4)	3.5229(7)	0.0404	35.7	83.8	146.2	6.8	$3.5 \times 10^5$	$2.7 \times 10^4$
30	3.0731(9)	3.5214(7)	0.0460	35.8	79.6	131.9	6.7	$4.0 \times 10^5$	$2.6 \times 10^4$

<sup>a</sup>Extrapolation from measured lattice parameters (Ref. 12).

composition of  $\text{C}_4\text{H}_6\text{O}_5$  at low temperature. The increase in sintering temperature improves both the crystallinity and the C substitution for B. The former will increase  $T_c$ , while the latter will decrease  $T_c$ . As a compromise, these two opposing factors result in a high level of C substitution for B with a relatively small drop in  $T_c$ . The high-field  $J_c$ 's of the  $\text{MgB}_2+\text{C}_4\text{H}_6\text{O}_5$  samples were much higher than that of the undoped  $\text{MgB}_2$ . Specifically, it should be noted that the self-field  $J_c$  of  $\text{MgB}_2+\text{C}_4\text{H}_6\text{O}_5$  samples was not reduced at addition levels as high as 30 wt %  $\text{C}_4\text{H}_6\text{O}_5$ ; hence the connectivity between  $\text{MgB}_2$  grains was not affected by addi-

tion with  $\text{C}_4\text{H}_6\text{O}_5$ . Although there is a possibility of the formation of  $\text{H}_2\text{O}$  during sintering due to the decomposition of  $\text{C}_4\text{H}_6\text{O}_5$ , there was no degradation in self-field  $J_c$ , even for 30 wt %  $\text{C}_4\text{H}_6\text{O}_5$  added to  $\text{MgB}_2$ . This may be attributable to the fact that the decomposition products, C and CO, of  $\text{C}_4\text{H}_6\text{O}_5$  reduced  $\text{B}_2\text{O}_3$  and hence increased the effective cross section of the superconductor.

Figure 1(a) shows the magnetic field dependence of  $J_c$  in all samples at 20 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  $2.5 \times 10^4 \text{ A cm}^{-2}$  at 5 K and 8 T for  $\text{MgB}_2+30 \text{ wt \% C}_4\text{H}_6\text{O}_5$  sample is higher than that of the undoped  $\text{MgB}_2$  by a factor of 21. In addition, there was no  $J_c$  degradation in self-field for the  $\text{MgB}_2+30 \text{ wt \% C}_4\text{H}_6\text{O}_5$  sample. These findings can be further supported by the flux pinning results. Figure 1(b) plots the field dependence of the volume pinning force,  $F_p=J \times B$ , of all samples at 20 K. The  $F_p$  is normalized by the maximum volume pinning force  $F_{p,\text{max}}$ . The flux pinning for the  $\text{MgB}_2+\text{C}_4\text{H}_6\text{O}_5$  samples was significantly higher than that of the undoped one at  $B > 1.5 \text{ T}$ . This result indicates that the  $F_p(B)$  of  $\text{MgB}_2+\text{C}_4\text{H}_6\text{O}_5$  samples was improved by the C substitution effect and nano-C inclusions within the grains.

The normalized temperature dependence of  $H_{\text{irr}}$  and  $H_{c2}$  for all samples is shown in Fig. 2. Significantly enhanced  $H_{\text{irr}}$  and  $H_{c2}$  for  $\text{MgB}_2+\text{C}_4\text{H}_6\text{O}_5$  samples were observed, suggesting that C substitution into B sites results in an enhancement in  $H_{\text{irr}}$  and  $H_{c2}$ . The steeper slopes of  $H_{\text{irr}}$  for  $\text{MgB}_2+\text{C}_4\text{H}_6\text{O}_5$  samples exceeded  $H_{c2}$  of undoped  $\text{MgB}_2$  below a

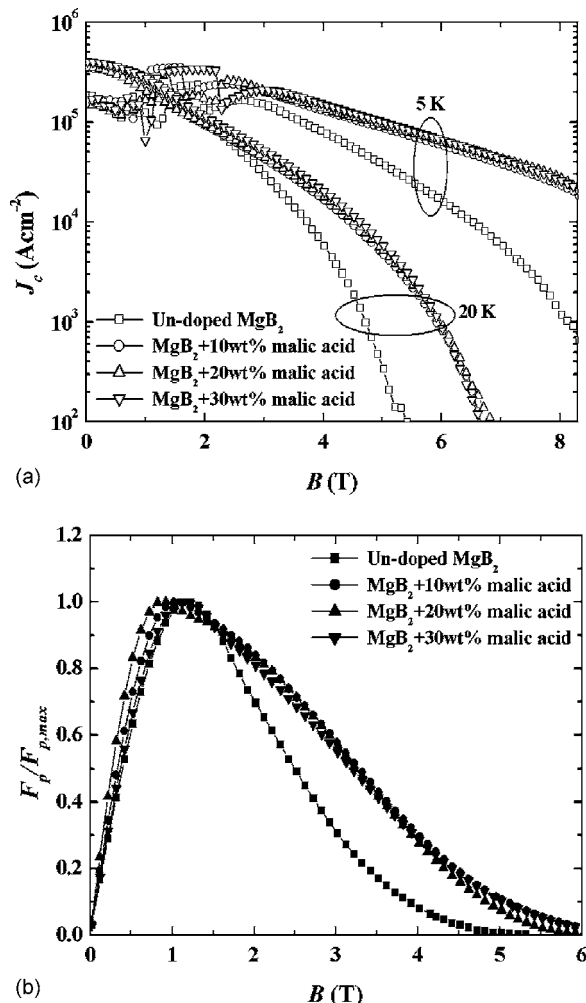


FIG. 1. Superconducting properties of undoped  $\text{MgB}_2$  and  $\text{MgB}_2+\text{C}_4\text{H}_6\text{O}_5$  samples with different addition levels: (a) Magnetic field dependence of  $J_c$  in all samples at 20 and 5 K; (b) field dependence of the volume pinning force,  $F_p=J \times B$ , of all samples at 20 K. The  $F_p$  is normalized by the maximum volume pinning force  $F_{p,\text{max}}$ .

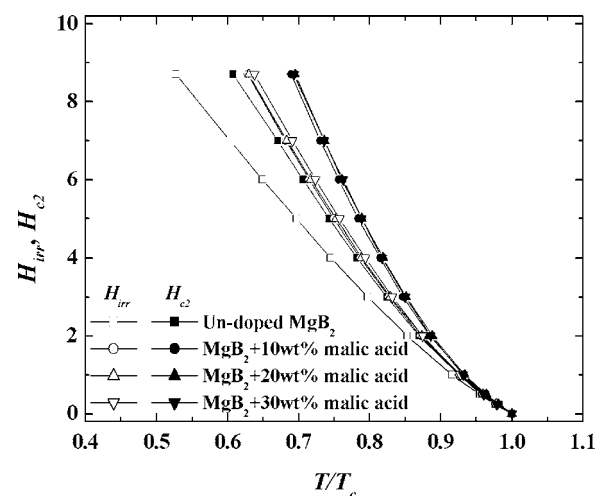


FIG. 2. Normalized temperature dependence of  $H_{\text{irr}}$  and  $H_{c2}$  for undoped and  $\text{C}_4\text{H}_6\text{O}_5$  doped samples.  $H_{c2}$  and  $H_{\text{irr}}$  were defined as  $H_{c2}=0.9R(T_c)$  and  $H_{\text{irr}}=0.1R(T_c)$  from the  $R$  vs  $T$  curve.

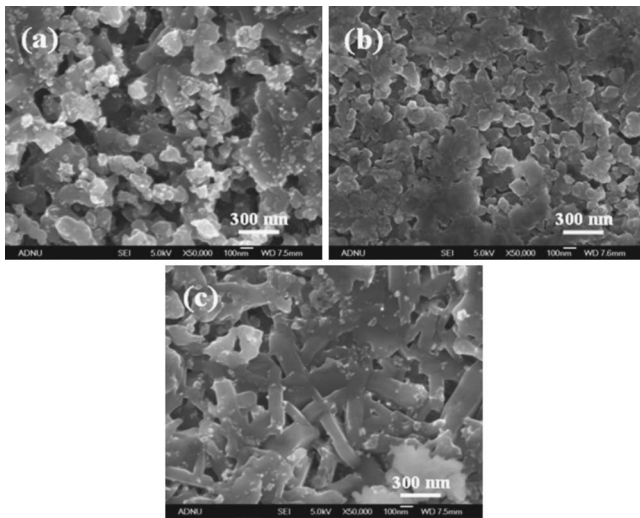


FIG. 3. Photographs from FEG-SEM: (a) Undoped  $\text{MgB}_2$ , (b)  $\text{MgB}_2$  + 10 wt %  $\text{C}_4\text{H}_6\text{O}_5$ , and (c)  $\text{MgB}_2$  + 30 wt %  $\text{C}_4\text{H}_6\text{O}_5$ .

temperature of 22 K. The resistivities  $\rho$  for the undoped and  $\text{MgB}_2 + \text{C}_4\text{H}_6\text{O}_5$  samples are 34 and 80–90  $\mu\Omega$  cm at 40 K, respectively, as shown in Table I. The increased resistivity for  $\text{MgB}_2 + \text{C}_4\text{H}_6\text{O}_5$  samples indicates the increased impurity scattering as a result of C substitution into B sites.

FEG-SEM images for (a) undoped  $\text{MgB}_2$ , (b)  $\text{MgB}_2$  + 10 wt %  $\text{C}_4\text{H}_6\text{O}_5$ , and (c)  $\text{MgB}_2$  + 30 wt %  $\text{C}_4\text{H}_6\text{O}_5$  are shown in Fig. 3. The undoped  $\text{MgB}_2$  sample appears inhomogeneous, consisting of crystalline grains from several tens of nanometers in size to 500 nm. The morphology of the  $\text{MgB}_2$  + 10 wt %  $\text{C}_4\text{H}_6\text{O}_5$  sample was refined to smaller, denser, and more homogeneous grains compared to the undoped  $\text{MgB}_2$  one. The grain refinement by 10 and 20 wt %  $\text{C}_4\text{H}_6\text{O}_5$  additions is supported by the full width at half maximum (FWHM) results for all the peaks, as shown in Fig. 4. As the doping level further increases to 30 wt %, however, grains appear to have a bar/plate shape, with their width up to 150 nm and length up to 400 nm, in a well connected grain network [Fig. 3(c)]. Consistent with the FEG-SEM image is the decrease in FWHM for the 30 wt % doped sample (Fig. 4) although the average FWHM values for all peaks are still bigger than those of the undoped sample. The FEG-SEM image suggests that at higher addition levels  $\text{C}_4\text{H}_6\text{O}_5$  may act as a sintering aid to improve the crystallinity. The grain growth should not improve the electromagnetic properties. However, this effect may be offset by the increase in C substitution level, the reduction in resistivity (Table I), and improvement in grain connectivity. This is well evidenced by the fact that the self-field  $J_c$  of the  $\text{MgB}_2$  + 30 wt %  $\text{C}_4\text{H}_6\text{O}_5$  sample was enhanced while the improved in-field  $J_c$ ,  $H_{\text{irr}}$ , and  $H_{c2}$  were maintained, as shown in Figs. 1 and 2.

In summary, carbohydrate doping results in a small depression in  $T_c$  but significantly increases the C substitution

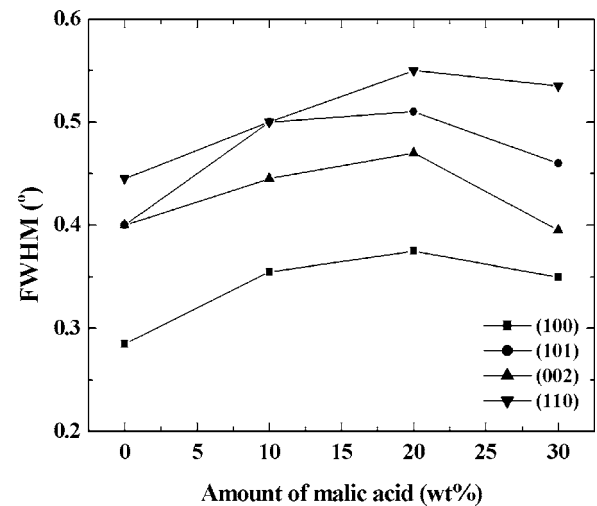


FIG. 4. FWHM as a function of the amount of  $\text{C}_4\text{H}_6\text{O}_5$ .  $\text{MgB}_2$ (100), (101), (002), and (110) correspond to  $2\theta \sim 33.6^\circ$ ,  $42.5^\circ$ ,  $52.0^\circ$ , and  $60.0^\circ$ , respectively.

level, reduces the impurities, and hence improves  $J_c$ ,  $H_{\text{irr}}$ , and  $H_{c2}$  performances at all the operating temperatures and over the entire field range. This finding opens a direction for the manufacture of nanodoped materials using the carbohydrate solution route, which solves the agglomeration problem, avoids the use of expensive nanoadditives, and achieves improved performance properties.

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- <sup>1</sup>J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, and J. Akimitsu, *Nature (London)* **410**, 63 (2001).
- <sup>2</sup>S. X. Dou, S. Soltanian, J. Horvat, X. L. Wang, S. H. Zhou, M. Ionescu, H. K. Liu, P. Munroe, and M. Tomsic, *Appl. Phys. Lett.* **81**, 3419 (2002).
- <sup>3</sup>J. H. Kim, W. K. Yeoh, M. J. Qin, X. Xu, and S. X. Dou, *J. Appl. Phys.* **100**, 013908 (2006).
- <sup>4</sup>R. H. T. Wilke, S. L. Bud'ko, P. C. Canfield, D. K. Finnemore, R. J. Suplinskas, and S. T. Hannahs, *Phys. Rev. Lett.* **92**, 217003 (2004).
- <sup>5</sup>H. Kumakura, H. Kitaguchi, A. Matsumoto, and H. Hatakeyama, *Appl. Phys. Lett.* **84**, 3669 (2004).
- <sup>6</sup>A. Yamamoto, J. I. Shimoyama, S. Ueda, I. Iwayama, S. Horii, and K. Kishio, *Supercond. Sci. Technol.* **18**, 1323 (2005).
- <sup>7</sup>Y. Bugoslavsky, G. K. Perkins, X. Qi, L. F. Cohen, and A. D. Caplin, *Nature (London)* **410**, 561 (2001).
- <sup>8</sup>R. Flükiger, H. L. Suo, N. Musolino, C. Beneduce, P. Toulemonde, and P. Lezza, *Physica C* **385**, 286 (2003).
- <sup>9</sup>A. Serquis, L. Civalde, D. L. Hammon, X. Z. Liao, J. Y. Coulter, Y. T. Zhu, M. Jaime, D. E. Peterson, and F. M. Mueller, *Appl. Phys. Lett.* **82**, 2847 (2002).
- <sup>10</sup>H. Yamada, M. Hirakawa, H. Kumakura, and H. Kitaguchi, *Supercond. Sci. Technol.* **19**, 175 (2006).
- <sup>11</sup>M. D. Sumption, M. Bhatia, M. Rindfleisch, M. Tomsic, S. Soltanian, S. X. Dou, and E. W. Collings, *Appl. Phys. Lett.* **86**, 092507 (2005).
- <sup>12</sup>S. Lee, T. Masui, A. Yamamoto, H. Uchitama, and S. Takama, *Physica C* **397**, 7 (2003).