2012

The effect of reduced graphene oxide addition on the superconductivity of MgB₂

K S. B De Silva

University of Wollongong, kaludewa@uow.edu.au

S Gambhir

University of Wollongong, sanjeev@uow.edu.au

Xiaolin Wang

University of Wollongong, xiaolin@uow.edu.au

X Xu

University of Wollongong, xun@uow.edu.au

W X. Li

University of Wollongong, wenxian@uow.edu.au

See next page for additional authors

Follow this and additional works at: <https://ro.uow.edu.au/engpapers>

Part of the [Engineering Commons](#)

<https://ro.uow.edu.au/engpapers/4851>

Recommended Citation

De Silva, K S. B; Gambhir, S; Wang, Xiaolin; Xu, X; Li, W X.; Officer, David L.; Wexler, D; Wallace, G G.; and Dou, S. X.: The effect of reduced graphene oxide addition on the superconductivity of MgB₂ 2012, 13941-13946.

<https://ro.uow.edu.au/engpapers/4851>

Authors

K S. B De Silva, S Gambhir, Xiaolin Wang, X Xu, W X. Li, David L. Officer, D Wexler, G G. Wallace, and S. X. Dou

The effect of reduced graphene oxide addition on the superconductivity of MgB_2 K. S. B. De Silva,^{*a} S. Gambhir,^{*b} X. L. Wang,^a X. Xu,^a W. X. Li,^a D. L. Officer,^b D. Wexler,^a G. G. Wallace^b and S. X. Dou^a

Received 17th January 2012, Accepted 9th May 2012

DOI: 10.1039/c2jm30323j

Reduced graphene oxide (rGO) and highly reduced chemically converted graphene (rCCG) samples were prepared under different processing conditions and were doped into MgB_2 by a diffusion process at 800 °C for 10 hours. It was demonstrated that a small addition rCCG can significantly improve the superconducting properties of MgB_2 . Doping of MgB_2 with 1 mol% of rCCG resulted in a J_c of $5.45 \times 10^5 \text{ A cm}^{-2}$ at 20 K in self-fields, which is nearly 32% improvement over that of the undoped sample. This is a significant improvement as most carbon sources adversely affect the J_c performance at the zero field.

Introduction

Since the discovery of superconductivity in MgB_2 ,¹ numerous efforts have been focussed on enhancing its superconducting properties, such as its critical current density (J_c), upper critical field (H_{c2}), and irreversibility field (H_{irr}). Compared to other low temperature superconductors, MgB_2 's high critical temperature (T_c) allows it to be used in liquid-cryogen-free systems. However, its rapid drop of critical current with applied magnetic fields and low critical fields excludes it from many commercial applications where high J_c in magnetic fields is required. Until today, one of the biggest challenges in MgB_2 research has been to improve H_{c2} and J_c in all field regions at the same time. As reported by many groups, carbon doping is a relatively simple and effective way of improving superconducting properties in MgB_2 .^{2–10} Various types of carbon sources have been used as dopants for MgB_2 , and J_c and H_{c2} have been significantly enhanced due to charge carrier scattering, thanks to the two-band nature of MgB_2 . Graphene is becoming recognized as a novel dopant for MgB_2 due to its specific way of improving J_c , as it improves the intergrain connectivity, and at the same time, leaves micro-strains in the MgB_2 matrix which are beneficial for improving the flux pinning.^{11,12}

There have been different procedures reported for the reduction of graphene oxide (GO), including chemical reduction, thermal annealing, microwave irradiation, *etc.*^{13–17} Generally, GO refers to the exfoliated graphite oxide, existing in the form of

single or few layer sheets. Hydrazine and its derivatives are reported as effective reducing agents for preparation of chemically converted graphene (CCG). It was recently reported that, some sulphur-containing compounds such as NaHSO_3 , $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, SOCl_2 , $\text{Na}_2\text{S}_2\text{O}_3$, and SO_2 can be used as reducing agents to reduce GO in aqueous solutions.¹⁶ However, the carbon to oxygen ratio of the end product totally depends on the method of preparation and the degree of reduction.¹⁸ Therefore, the aim of this study is to understand the effectiveness of the novel two-stage reduction process in reducing GO and the effects of these carbon additives on improving the superconducting properties of MgB_2 .

Results and discussion

The XRD analysis for GO and RGOs is shown in Fig. 1. A typical broad peak near $2\theta = 9.86^\circ$, corresponding to a layer-to-layer

Fig. 1 XRD patterns of GO, rCCG and rGO samples.

^aInstitute for Superconducting and Electronic Materials, University of Wollongong, Northfields Avenue, Wollongong, New South Wales, 2522, Australia. E-mail: ksbs664@uowmail.edu.au

^bARC Centre of Excellence for Electromaterials Science and Intelligent Polymer Research Institute, University of Wollongong, Northfields Avenue, Wollongong, New South Wales, 2522, Australia. E-mail: sanjeev@uow.edu.au

distance (d -spacing) of ~ 0.896 nm, was observed for the GO powder. A dramatic shift to higher 2θ angles ($\sim 25.56^\circ$ and 25.47°) with decreased d -spacing of ~ 0.349 and 0.348 nm respectively was observed for rGO and rCCG samples. This reduction of the d -spacing clearly indicates a better ordering of the two-dimensional structure.¹⁴ The results from the XPS analysis are shown in Fig. 2. The high resolution C1s spectra are compared between the GO sheets obtained before and after reduction. The GO spectrum, given in Fig. 2(a), was deconvoluted into four peaks corresponding to the following functional groups: C=C/C-C (284.9 eV), C-O (hydroxyl and epoxy, 286.7 eV), C=O (carbonyl, 287.4 eV) and O=C-O (carboxyl 287.9 eV). The C1s spectrum of rGO in Fig. 2(b) represents four environments corresponding to carbon atoms in different functional groups and assigned as C=C (sp^2 , 284.4 eV), C-C (sp^2 , 285.4 eV), C-O (286.3 eV), and C=O (carbonyl, 288.1 eV).^{16,19} The C1s peaks in the XPS reveal that most of the oxygen containing functional groups were significantly reduced during the reduction of GO using either of the two reduction procedures. Although all the above peaks are visible for rCCG in Fig. 2(c), the intensities have become much smaller after the two-step reduction treatment. The minor peak at 290.7 eV was identified as acid chloride, which might be occurring due to the treatment with $SOCl_2$.²⁰ The atomic percentages as depicted by

Fig. 2 High resolution C1s spectra of: (a) GO, (b) rGO and (c) rCCG.

Fig. 3 XRD patterns of undoped, rGO- and rCCG-doped MgB_2 .

XPS for rCCG were 87.61% C and 6.73% O (or by mass, 85.33% C and 8.74% O). The same analysis for rGO was 82.62% C and 13.26% O by atomic composition (or by mass, 74.77% C and 15.99% O).

According to the XRD patterns presented in Fig. 3, it seems that all samples have a well-developed MgB_2 phase. Among the various XRD peaks, the full width at half maximum (FWHM) of (110) is related to the in-plane crystallinity. Therefore, FWHM analysis provides considerable information on grain size and lattice strain in the sample. Micro-strain occurs due to the presence of lattice defects, resulting in peak broadening, while macro-strain appears due to the C substitution at boron sites resulting in a peak shift.²¹ FWHM values of the (110) peak is visible as the doping level is very low, however, increased FWHM values of the (110) peak of the doped samples compared with the undoped sample give evidence for increased lattice strain due to doping.²¹

Fig. 4(a)–(c) show FESEM secondary electron images obtained from powders obtained by grinding undoped, rCCG-doped and rGO-doped samples respectively. The images indicate a rather homogeneous grain structure, with the apparent grain size around 200 nm. Compared to the undoped sample, the doped samples appear to have better grain connectivity and decreased porosity. The presence of a minor phase was also identified, particularly on the doped samples, and appears as a lighter grey contrast in the figures. EDS analysis confirmed the presence of Mg and B in both phases with a variation of the Mg : B ratio.

Preliminary transmission electron microscopy (TEM) investigations were performed on thin sample slices prepared by dual beam focussed ion beam milling (Fig. 5). A low magnification image of the rGO doped sample lifted out onto a quantifoil carbon support film is shown in Fig. 5(a). Regions of porosity (marked in Fig. 5(a)) were not quantified, but appeared greater in the undoped MgB_2 sample than in the other two. Contrast consistent with the presence of MgB_2 was obtained from high resolution images, such as that shown in the image inset in Fig. 5(c), which can be attributed to lattice planes perpendicular to the c lattice direction. A significant difference between the

Fig. 4 FESEM image of powdered samples of: (a) undoped, (b) rCCG- and (c) rGO-doped MgB_2 .

Fig. 5 TEM images of samples prepared by focussed ion beam milling: (a–c) rGO doped, (d) undoped MgB_2 , and (e and f) rCCG doped samples.

undoped MgB_2 , and the rCCG-doped and rGO-doped samples was evident in motley contrast, marked in Fig. 5(b) and (f), consistent with a carbon containing coating distributed throughout the MgB_2 . This contrast was absent in the undoped sample (Fig. 5(d)). Additional diffraction and high resolution investigations are required to fully characterise both the MgB_2 and the reduced graphene oxide morphology and its distribution throughout the doped samples. However, we believe that the presence of the reduced graphene evident in both rCCG-doped and rGO doped samples plays an important role in promoting grain connectivity and, thereby, improved superconducting properties.

Fig. 6 Raman spectra with Gaussian fitted E_{2g} mode and PDOS distortion of undoped, rGO- and rCCG-doped MgB_2 .

Raman studies were carried out on these samples at room temperature in the range of 300 to 1000 cm^{-1} and are shown in the Fig. 6. Owing to the simple hexagonal structure (space group $P6/mmm$), four optical modes at the Γ point of the Brillouin zone are predicted for MgB_2 : a silent B_{1g} mode (at 87.1 meV, $\sim 700 \text{ cm}^{-1}$), the E_{2g} Raman mode (at 74.5 meV, $\sim 600 \text{ cm}^{-1}$), the infrared active E_{2u} (at 40.7 meV, $\sim 330 \text{ cm}^{-1}$), and A_{2u} (at 49.8 meV, $\sim 400 \text{ cm}^{-1}$).²² There are two peaks in the measured range centered at about 600 cm^{-1} and 775 cm^{-1} . The low frequency Raman band is assigned to the E_{2g} mode, which is Raman active while the high frequency band is attributed to the phonon density of states (PDOS) due to disorder. Therefore, the electron–phonon coupling intensity and the crystal distortion will influence the Raman shift and the line width of the Raman scattering.^{22,23} As revealed by Fig. 6, a slight shift of the E_{2g} band to the low frequency range can be observed in doped samples when compared with the undoped sample, which gives an evidence of induced tensile strain as a result of doping.^{11,22} The PDOS band becomes more prominent in doped samples, indicating an increased disorder due to doping.²²

The magnetic critical current densities (J_c) of undoped, rGO-, and rCCG-doped MgB_2 bulk samples as a function of applied magnetic field are shown in Fig. 7. The J_c performances of doped samples improved significantly under both low and high fields, even with only a small amount of doping (1 mol%). At zero field and 20 K, J_c 's of the undoped, rGO, and rCCG doped samples are $4.1 \times 10^5 \text{ A cm}^{-2}$, $5.15 \times 10^5 \text{ A cm}^{-2}$, and $5.45 \times 10^5 \text{ A cm}^{-2}$, respectively. This is quite remarkable, as many carbon dopants have an adverse effect on J_c in the low field region. According to Eisterer,²⁴ the connectivity is a major factor which governs the

Fig. 7 In-field J_c performance of undoped, rGO- and rCCG-doped MgB_2 bulk samples.

Table 1 Critical temperature (T_c), residual resistivity ratio (RRR), difference in resistivity at 300 K and 40 K, and active cross-sectional area (A_F) of the undoped, rGO- and rCCG doped MgB_2 bulk samples

Sample	T_c (K)	RRR	$\Delta\rho$ (300–40 K) ($\mu\Omega$ cm)	A_F
Undoped	38.89	3.90	34.00	0.126
rGO doped	38.39	3.32	29.98	0.143
rCCG doped	38.56	3.45	21.28	0.202

self-field J_c . Therefore, improved connectivity is responsible for the high values of J_c at zero field for the doped MgB_2 samples. The presence of the highest amount of carbon through an effective reduction process could be associated with the best J_c performance at low fields, by the rCCG doped sample. The same sample shows a significant improvement in critical current density in high fields, nearly a 6.5 times improvement at 5 K and 8 T compared to undoped samples. The critical current density in high fields near H_{c2} is mainly governed by H_{c2} , and hence higher H_{c2} leads to a higher J_c . This, together with the improved connectivity, explains why the highest J_c performance is observed in the rCCG doped MgB_2 in high fields.²⁵

Table 1 summarizes the critical temperature, residual resistivity ratio (RRR), difference in resistivities at 40 K and 300 K ($\Delta\rho$), and active cross-section (A_F) for the undoped and doped MgB_2 bulk samples. Only a slight decrease in T_c , nearly 0.5 K, is observed due to doping. This is a remarkable feature in graphene doping as most of the carbon sources are associated with a higher T_c reduction,²⁶ however, there are other parameters also affecting the T_c such as doping level and sintering temperature. Therefore, low level of doping and the sintering conditions would also have prevented the T_c reduction in this study. The normal state resistivity variation with temperature is given in Fig. 8 and the inset shows the normalized resistivity variation with temperature. The rCCG doped sample shows a reduction in resistivity, while the undoped and rGO doped samples show similar resistivities. However, this reduction in resistivity is in contrast with the

Fig. 8 Resistivity variation with temperature of undoped, rGO- and rCCG-doped MgB_2 bulk samples. The inset shows the variation of the normalized resistivity with temperature.

results of general carbon doping, which tends to increase the resistivity after doping, due to increased interband and intraband scattering in the σ -bands.²⁷ In addition to that, as explained by Rowell,²⁷ connectivity also plays a major role in determining the resistivity of MgB_2 . Therefore, better connectivity, which means higher A_F values, indicates broad channels of supercurrents. The increased A_F values reveal that the intergrain connectivity has been improved due to doping, irrespective of the production route; however the rCCG doped sample shows a better improvement than the rGO doped one. Increased electrical conductivity, the less defective structure, lesser oxygen amount present in the sample and improved density may have resulted in a higher A_F for this sample. The RRR, *i.e.*, the ratio of the resistivity at 300 K to that at 40 K, reflects the degree of electron scattering. When the electron scattering is high, it causes a reduction in the RRR. The obtained RRR values for the graphene doped samples are smaller than that of the undoped sample and are therefore in a good agreement with the literature.^{27,28} For further analysis of the temperature dependence of the normal state resistivity, normalized resistivity values were fitted with the following equation, $\rho(T) = \rho_0 + aT^n$, where ρ_0 is the residual resistivity and n is the power law dependence of the resistivity.²⁹ The inset of Fig. 8 shows that the experimental data for undoped, rGO- and rCCG doped samples were well fitted with the above equation over the temperature range between T_c and 300 K. For the undoped sample, the parameter values obtained from this fit are $\rho_0 = 0.223 \mu\Omega$ cm, $a = 2.671 \times 10^{-6} \mu\Omega$ cm K^{-n} , and $n = 2.19$. The parameter values obtained for the rGO-doped sample from this fit are $\rho_0 = 0.286 \mu\Omega$ cm, $a = 4.96 \times 10^{-6} \mu\Omega$ cm K^{-n} , and $n = 2.07$. The parameter values obtained for the rCCG-doped sample from this fit are $\rho_0 = 0.251 \mu\Omega$ cm, $a = 2.87 \times 10^{-6} \mu\Omega$ cm K^{-n} , and $n = 2.17$. The changes in the n values can be attributed to the disorder due to doping, as the disorder leads to reduce the value of n .²⁹ These fitted results together with the RRR values confirm the disorder occurred due to doping. Therefore, the variations in the resistivity of undoped and doped samples depend on the combined effect of the connectivity factor and the effects of disorder.

Fig. 9 Schematic of the synthesis of rGO and rCCG.

Conclusions

A study of the effects of reduced graphene oxide doping on the superconducting properties of MgB_2 has been conducted. It was found that the modified conditions of reduction that improved first reduction of GO using hydrazine followed by the SOCl_2 treatment resulted in significant improvements in critical current density in a wide range of fields, and very low resistivity for the rCCG-doped MgB_2 samples. Improvements in critical current density of all doped samples are mainly attributed to improved intergrain connectivity, which is a salient feature in graphene doping. According to our results, rCCG synthesised through this novel two-step reduction process is a promising dopant which can effectively improve the superconducting properties of MgB_2 without much depression of T_c .

Experimental

Sample preparation

Preparation of rGO and rCCG. *rGO*: GO was prepared and purified according to the modified Hummers method,³⁰ and treated with thionyl chloride (SOCl_2) by drying the aqueous dispersion of GO by azeotropic distillation using benzene overnight, resulting in solid GO agglomerates in the flask, which were further dried under vacuum at 60°C for 48 hours. The dried GO was finally ground into powder and this powder GO (500 mg) was treated with an excess of SOCl_2 in 1,2-dichloroethane for 2 h. After complete removal of solvent and SOCl_2 , the suspended rGO was washed with dichloromethane (DCM) and dried under vacuum overnight at 60°C to remove all traces of SOCl_2 .

rCCG: An aqueous dispersion of the chemically converted graphene (CCG) aqueous dispersion was first obtained as per the procedure reported by Li *et al.* through oxidation of graphite to GO.^{15,16} Highly reduced CCG (rCCG) was obtained by treating an aqueous dispersion of CCG (1.0 l, 0.5 mg ml^{-1}) with 2 ml of hydrazine (65%) at refluxing temperature for 2 h, followed by cooling to 50°C . Dilute sulphuric acid (5%) was added dropwise, until the pH was 2–3. This resulted in agglomeration of the graphene dispersion in less than two hours. These agglomerates were filtered, washed with Milli-Q water, and dried at 50°C under vacuum overnight, resulting in rCCG (0.47 g). These fine agglomerates of rCCG (220 mg) were further treated with an excess quantity of SOCl_2 for two hours at 70°C .¹³ The excess SOCl_2 was removed by washing with DCM and drying the powder under vacuum overnight, resulting in a quantitative yield

of rCCG. Fig. 9 elaborates the chemical route to the synthesis of rGO and rCCG samples.

Fabrication of MgB_2 bulk samples

Graphene doped bulk samples were prepared by the diffusion method with crystalline boron powder (0.2 to $2.4\ \mu\text{m}$) 99.999%, Mg powder (99%, 352 mesh) and differently produced graphene as precursors. Initially boron was mixed with rGO and rCCG powders in a mortar separately, according to the formula $\text{MgB}_{1.99}\text{C}_{0.01}$. Powders were then pressed into pellets 13 mm in diameter, and then inserted into a soft iron tube with the stoichiometric ratio of Mg with 20% excess to compensate for the loss of Mg during sintering. The samples were sintered at 800°C for 10 h in a quartz tube at the heating rate of 5°C min^{-1} under high purity argon (Ar 99.9%) gas.

Characterization

The phase identification and crystal structure investigations were carried out at room temperature using an X-ray diffractometer (GBCMMA) with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54059\ \text{\AA}$). X-ray photoelectron spectroscopy was conducted using an ESCA-LAB220i-XL instrument manufactured by Thermo Scientific (originally VG Scientific, UK) with vacuum less than 2×10^{-9} mbar. The X-ray source used was Al $\text{K}\alpha$ (energy 1486.6 eV) at 400 W (27 mA and 15 kV). A JEOL JSM-7500FA Field Emission Scanning Electron Microscope (FESEM), equipped with an Ultra-Thin Window (UTW) JEOL hyper-minicup Energy Dispersive Spectrometer (EDS) was used for SEM analysis. Transmission electron microscopy was performed using a JEOL 3000F field emission instrument located at the University of Sydney. TEM samples were prepared from solid samples by the Dual Beam FIB technique (FEI xT Nova NanoLab 200 Nova instrument, University of New South Wales) with thin slices lifted out onto the quantifoil carbon support film. The Raman scattering was measured using a confocal laser Raman spectrometer (HORIBA Jobin Yvon system) with a $100\times$ microscope. The 632.8 nm line of a HeNe laser with power of about 20 mW was used for excitation. The critical temperature (T_c) was determined from the ac susceptibility measurements, and the magnetic J_c was derived from the width of the magnetization loops, obtained with a quantum design physical properties measurement system (PPMS) using Bean's model.³¹ The resistivity measurements were conducted using the standard dc four-probe technique under magnetic fields up to 13 T. The

active cross-section (A_F) was calculated from the resistivity, ρ , from Rowell's model.²⁷

Acknowledgements

This research was performed with the financial support of the Australian Research Council (ARC) through project DP0770205, LP0989352. The authors would like to thank ANFF Materials node for material supply and characterisation and Dr T. Silver, for helpful discussions. The authors also acknowledge the support and assistance of Mr Tony Romeo and Mr Darren Attard from the Wollongong University Electron Microscopy Centre. We also acknowledge the facilities and the scientific and technical assistance of the Australian Microscopy & Microanalysis Research Facility, TEM instrument training from Mr Shaun Bulcock from the University of Sydney, and preparation of FIB samples from Dr Chung Kong from the University of New South Wales. This work was supported by Hyper Tech Research Inc., Oh, USA and the University of Wollongong.

References

- 1 J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani and J. Akimitsu, *Nature*, 2001, **410**, 63.
- 2 R. H. T. Wilke, S. L. Bud'ko, P. C. Canfield, D. K. Finnemore, R. J. Suplinskas and S. T. Hannahs, *Phys. Rev. Lett.*, 2004, **92**, 217003.
- 3 S. X. Dou, A. V. Pan, S. Zhou, M. Ionescu, X. L. Wang, J. Horvat, H. K. Liu and P. R. Munroe, *J. Appl. Phys.*, 2003, **94**, 1850.
- 4 B. J. Senkowitz, J. E. Giencke, S. Patnaik, C. B. Eom, E. E. Hellstrom and D. C. Larbalestier, *Appl. Phys. Lett.*, 2005, **86**, 202502.
- 5 P. Lezza, C. Senatore and R. Flukier, *Supercond. Sci. Technol.*, 2006, **19**, 1030.
- 6 A. Serquis, G. Serrano, S. M. Moreno, L. Civale, B. Maiorov, F. Balakirev and M. Jaime, *Supercond. Sci. Technol.*, 2007, **20**, L12.
- 7 E. W. Collings, M. D. Sumption, M. Bhatia, M. A. Susner and S. D. Bohnenstiehl, *Supercond. Sci. Technol.*, 2008, **21**, 103001.
- 8 C. Buzea and T. Yamashita, *Supercond. Sci. Technol.*, 2001, **14**, R115.
- 9 Y. Ma, X. Zhang, G. Nishijima, K. Watanabe, S. Awaji and X. Bai, *Appl. Phys. Lett.*, 2006, **88**(7), 072502.
- 10 X. Zhang, Y. Ma, Z. Gao, D. Wang, L. Wang, W. Liu and C. Wang, *J. Appl. Phys.*, 2008, **103**(10), 103915.
- 11 K. S. B. De Silva, X. Xu, S. Gambhir, X. L. Wang, W. X. Li, G. G. Wallace and S. X. Dou, *Scr. Mater.*, 2011, **65**, 634.
- 12 X. Xu, S. X. Dou, X. L. Wang, J. H. Kim, J. A. Stride, M. Choucair, W. K. Yeoh, R. K. Zheng and S. P. Ringer, *Supercond. Sci. Technol.*, 2010, **23**, 085003.
- 13 G. Eda, Y.-Y. Lin, S. Miller, C.-W. Chen, W.-F. Su and M. Chhowalla, *Appl. Phys. Lett.*, 2008, **92**, 233305.
- 14 I. K. Moon, J. Lee, R. S. Ruoff and H. Lee, *Nat. Commun.*, 2010, **1**, 73.
- 15 D. Li, M. B. Muller, S. Gilje, R. B. Kaner and G. G. Wallace, *Nat. Nanotechnol.*, 2008, **3**, 101.
- 16 W. Chen, L. Yan and P. R. Bangal, *J. Phys. Chem. C*, 2010, **114**, 19885.
- 17 W. Chen, L. Yan and P. R. Bangal, *Carbon*, 2010, **48**(4), 1146.
- 18 I. Jung, D. A. Field, N. J. Clark, Y. Zhu, D. Yang, R. D. Piner, S. Stankovich, D. A. Dikin, H. Geisler, C. A. Ventrice and R. S. Ruoff, *J. Phys. Chem. C*, 2009, **113**, 18480.
- 19 A. F. Perez-Cadenas, F. J. Maldonado-Hodar and C. Moreno-Castilla, *Carbon*, 2003, **41**, 473.
- 20 T. A. Carlson, *X-ray Photoelectron Spectroscopy*, Dowden, Hutchinson & Ross, Stroudsburg, PA, 1978.
- 21 J. H. Kim, S. X. Dou, J. L. Wang, D. Q. Shi, X. Xu, M. S. A. Hossain, W. K. Yeoh, S. Choi and T. Kiyoshi, *Supercond. Sci. Technol.*, 2007, **20**, 448.
- 22 W. X. Li, R. H. Chen, Y. Li, M. Y. Zhu, H. M. Jin, R. Zeng, S. X. Dou and B. Lu, *J. Appl. Phys.*, 2008, **103**(1), 013511.
- 23 W. X. Li, Y. Li, R. H. Chen, R. Zeng, M. Y. Zhu, H. M. Jin and S. X. Dou, *J. Phys.: Condens. Matter*, 2008, **20**(25), 255235.
- 24 M. Eisterer, *Supercond. Sci. Technol.*, 2007, **20**, R47.
- 25 Y. Zhang, X. Xu, Y. Zhao, J. H. Kim, C. Lu, S. H. Zhou and S. X. Dou, *Supercond. Sci. Technol.*, 2008, **21**, 115004.
- 26 W. X. Li, X. Xu, Q. H. Chen, Y. Zhang, S. H. Zhou, R. Zeng and S. X. Dou, *Acta Mater.*, 2011, **59**(19), 7268.
- 27 J. M. Rowell, *Supercond. Sci. Technol.*, 2003, **16**, R17.
- 28 X.-L. Wang, S. X. Dou, M. S. A. Hossain, Z. X. Cheng, X. Z. Liao, S. R. Ghorbani, Q. W. Yao, J. H. Kim and T. Silver, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2010, **81**, 224514.
- 29 I. M. Obaidat and B. A. Albiss, *Cryst. Res. Technol.*, 2008, **43**(1), 83.
- 30 N. I. Kovtyukhova, P. J. Ollivier, B. R. Martin, T. E. Mallouk, S. A. Chizhik, E. V. Buzaneva and A. D. Gorchinskiy, *Chem. Mater.*, 1999, **11**, 771.
- 31 C. P. Bean, *Rev. Mod. Phys.*, 1964, **36**, 31.