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# Effect of sintering temperature on the superconducting properties of graphene doped MgB<sub>2</sub>

## Abstract

A comprehensive study on the effects of sintering temperature on graphene-doped MgB<sub>2</sub> superconductor was conducted. Graphene has emerged as an effective dopant that is capable of improving the critical current density ( $J_c$ ) and flux pinning at a very low doping level, with only a slight reduction of the critical temperature ( $T_c$ ). MgB<sub>2</sub> undoped and graphene-doped bulk samples were prepared by the in situ method and sintered within a temperature range from 650 to 950 °C. It is surprising to note that at the doping level of 1 at.% the sample sintered at 850 °C shows a  $J_c$  of  $5.6 \times 10^3$  A/cm<sup>2</sup>, which is nearly two times higher than that of the undoped sample, with a slight reduction in  $T_c$  of 0.5 K. The effects of the sintering temperature on the lattice parameters, resistivity, grain to grain connectivity, lattice disorder, and critical fields have also been investigated. The results are compared with those for undoped samples subjected to the same sintering conditions, and the origins of the differences in the critical current density are discussed. 2002-2011 IEEE.

## Keywords

graphene, properties, superconducting, doped, temperature, effect, mgb2, sintering

## Disciplines

Engineering | Physical Sciences and Mathematics

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# Effect of sintering temperature on the superconducting properties of graphene doped $\text{MgB}_2$

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**Abstract-** A comprehensive study on the effects of sintering temperature on graphene doped  $\text{MgB}_2$  superconductor was conducted. Graphene has emerged as an effective dopant that is capable of improving the critical current density ( $J_c$ ) and flux pinning at a very low doping level, with only a slight reduction of the critical temperature ( $T_c$ ).

$\text{MgB}_2$  un-doped and graphene doped bulk samples were prepared by the in-situ method and sintered within a temperature range from 650 to 950 °C. It is surprising to note that at the doping level of 1 at. % the sample sintered at 850 °C shows a  $J_c$  of  $5.6 \times 10^3 \text{ A/cm}^2$ , which is nearly 2 times higher than that of the un-doped sample, with a slight reduction in  $T_c$  of 0.5 K. The effects of the sintering temperature on the lattice parameters, resistivity, grain to grain connectivity, lattice disorder, and critical fields have also been investigated. The results are compared with those for un-doped samples subjected to the same sintering conditions, and the origins of the differences in the critical current density are discussed.

**Index Terms**—resistivity, upper critical and irreversibility fields, magnetic critical current density,  $\text{MgB}_2$  bulk

## I. INTRODUCTION

Since the discovery of superconductivity in  $\text{MgB}_2$ , numerous efforts have been focused on enhancing its superconducting properties, such as its critical current density ( $J_c$ ), upper critical field ( $H_{c2}$ ), and irreversibility field ( $H_{irr}$ ) [1]. Besides having a high  $T_c$ , the simple crystal structure, large coherence length, high critical field, transparency of grain boundaries to supercurrent, and low product cost, are all fascinating features that have benefits for its use in both large-scale applications and electronic devices [2-4].

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The critical current density of pristine  $\text{MgB}_2$  drops rapidly in high magnetic field, however, due to the weak pinning centers and low upper critical field. Chemical doping is known to be the simplest way to improve the superconducting properties of  $\text{MgB}_2$  superconductors. Among the many dopants investigated, carbon dopants are at the forefront, due to their capacity for addressing the drawbacks to  $\text{MgB}_2$ , particularly in terms of improving the performance of  $J_c$  at high fields and improving the  $H_{c2}$  [3-6].

Graphene (G) is recognized as a novel dopant for  $\text{MgB}_2$  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  $\text{MgB}_2$  matrix, which are beneficial for improving the flux pinning at very low doping levels [7, 8]. The reported results on graphene doping are mostly based on samples prepared through the diffusion process, however, for industrial applications, it is necessary to analyze the performance of samples prepared in a similar manner to the powder-in-tube method, which is the most widely used method to make  $\text{MgB}_2$  wires.

In this study, we will present a systematic study on the effects of sintering temperature on the superconducting properties of graphene  $\text{MgB}_2$  bulk samples prepared through the in-situ method.

## II. EXPERIMENTAL METHODS

Un-doped and G-doped bulk samples were prepared via the in-situ method from crystalline boron powder (0.2 to 2.4  $\mu\text{m}$ , 99.999%), Mg powder (99%, 352 mesh), and highly reduced chemically converted graphene (rCCG) [9] as precursors. Powders were mixed by mortar and pestle, pressed in a uniaxial press and made into pellets 13 mm in diameter. All the doped samples were prepared by adding 1 at. % graphene. These pellets were sintered at four different temperatures, 650 °C, 750 °C, 850 °C, and 950 °C, respectively, for 30 minutes, at a heating rate of 5 °C/min, under high purity Ar atmosphere. The phase identification and crystal structure investigations were carried out using an X-ray diffractometer (XRD; GBCMMA) with Cu-K $\alpha$  radiation ( $\lambda = 1.54059 \text{ \AA}$ ). The scanning electron microscope (SEM) images were collected using a Zeiss Ultra Plus scanning electron microscope.

The superconducting transition temperature,  $T_c$ , was determined from the AC susceptibility measurements, and the magnetic  $J_c$  was derived from the width of the magnetization loop using Bean's model [10], with data collected by a Quantum Design physical properties measurement system

TABLE I Full width at half maximum (FWHM), intensity ratio of MgO to MgB<sub>2</sub>, critical temperature, resistivity at 300 K & 40 K, residual resistance ratio (RRR) and active cross-sectional area (A<sub>F</sub>) of the un-doped, and G-doped MgB<sub>2</sub> bulk samples prepared at different sintering temperatures.

Sample	FWHM (110) (°)	I <sub>MgO</sub> /I <sub>MgB<sub>2</sub></sub> (%)	T <sub>c</sub> (K)	ρ (300K) (μΩ cm)	ρ (40K) (μΩ cm)	RRR	A <sub>F</sub> (%)
Pure MgB <sub>2</sub> @ 750 °C	0.4560	9.67	36.8	129.62	61.73	2.099	6.33
Pure MgB <sub>2</sub> @ 850 °C	0.4320	10.06	37.4	120.91	56.87	2.126	6.71
Pure MgB <sub>2</sub> @ 950 °C	0.4140	8.18	37.8	121.1	48.43	2.500	5.91
G-doped MgB <sub>2</sub> @ 750 °C	0.4780	11.02	36.5	137.7	67.7	1.967	6.35
G-doped MgB <sub>2</sub> @ 850 °C	0.4720	10.62	37.1	122.07	61.73	1.977	7.12
G-doped MgB <sub>2</sub> @ 950 °C	0.4420	10.59	37.6	116.09	47.69	2.434	6.28

(PPMS). The resistivity measurements were conducted using the standard dc four-probe technique under magnetic fields up to 13 T. The upper critical field ( $H_{c2}$ ) and the irreversibility field ( $H_{irr}$ ) were determined using the 90% and 10% criteria of R(T) for different applied fields, where R(T) is the normal state resistance near 40 K. The active cross-section (A<sub>F</sub>) was calculated from the resistivity,  $\rho$ , from Rowell's model [11].

### III. RESULTS AND DISCUSSION

Analysis of the XRD patterns of the powdered samples showed that all samples (i.e. both un-doped and G-doped) consisted of a main phase of MgB<sub>2</sub> together with MgO as a minor phase (not shown). Mg peaks, however, were also observed in the samples sintered at 650° C, indicating the incomplete formation of MgB<sub>2</sub> under that sintering condition. No significant peak shift was observed for the samples, due to

the low doping level (1 at %). Table 1 summarizes the full width at half maximum (FWHM) of the (110) peak, the MgO level, the critical temperature ( $T_c$ ), the resistivity at 300 K and 40 K, the residual resistivity ratio (RRR), and the active cross-sectional area (A<sub>F</sub>) of un-doped and G-doped MgB<sub>2</sub> bulk samples.

Analysis of FWHM offers considerable information on the crystallite size and lattice strain in the sample. Among the XRD peaks, the FWHM of the (110) diffraction peak reveals information on the crystallinity. The grain size and the strain can alter the FWHM value [12]. The FWHM trend for the un-doped samples discloses the effects of the sintering temperature on the crystallinity. The G-doped samples are, however, affected by the contrary effects of both sintering temperature and substitution. The crystals of the doped samples have grown under strain due to the C substitution effect. The increased FWHM value of the (110) peak for the G-doped samples compared to the un-doped samples at relevant temperatures, gives evidence of strain effects that have occurred due to the changes in the in-plane crystallinity from graphene doping. It is hard to see any trend in the MgO levels of the samples with temperature, however, G-doped samples show higher levels compared to the un-doped samples. The presence of MgO is inevitable in samples prepared by the in-situ method, as Mg acts as an oxygen getter in air, due to its high reactivity.

Fig. 1 in panels (a), (b), and (c) shows the SEM images of the un-doped samples sintered at 750 °C, 850 °C, and 950 °C, respectively. Panels (d), (e), and (f) in Fig. 1 are SEM images of the G-doped samples with the same sintering temperatures. Porosity is clearly visible in almost all of the samples, however, it seems to be reduced in the samples which were sintered at high temperatures. Compared to amorphous boron, the reactivity of crystalline boron is low, and consequently sufficient heat energy is required to form homogeneous MgB<sub>2</sub> grains. The merging of several grains into a cluster is more visible in the samples that were sintered at higher temperatures. On the other hand, the grain structure and the morphology seem to be slightly different in the G-doped samples compared to the un-doped, as the former seem to have more homogeneous grains, and most of those grains have merged together into big clusters. A specific feature in graphene doping of MgB<sub>2</sub> is that it improves the inter-grain connectivity [7, 9].

The variation of  $T_c$ , with the sintering temperature (shown in Table 1) is in-line with the literature, as higher sintering

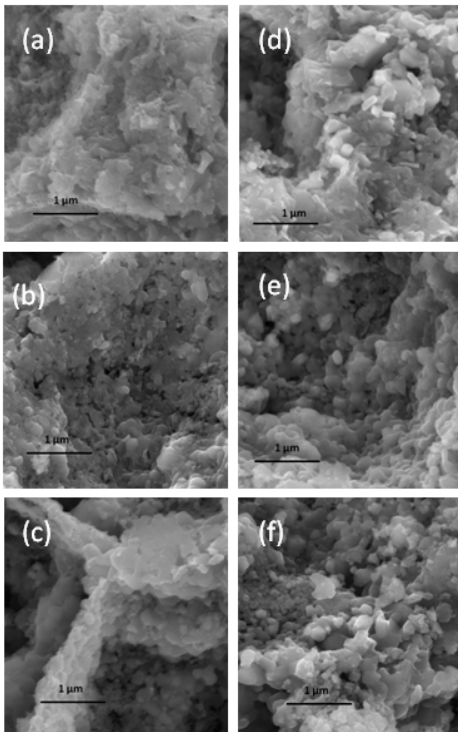


Fig. 1. SEM images of undoped (a-c) and G-doped (d-f) MgB<sub>2</sub> bulk samples sintered at 750 °C (a, d), 850 °C (b, e), and 950 °C (c, f) respectively.

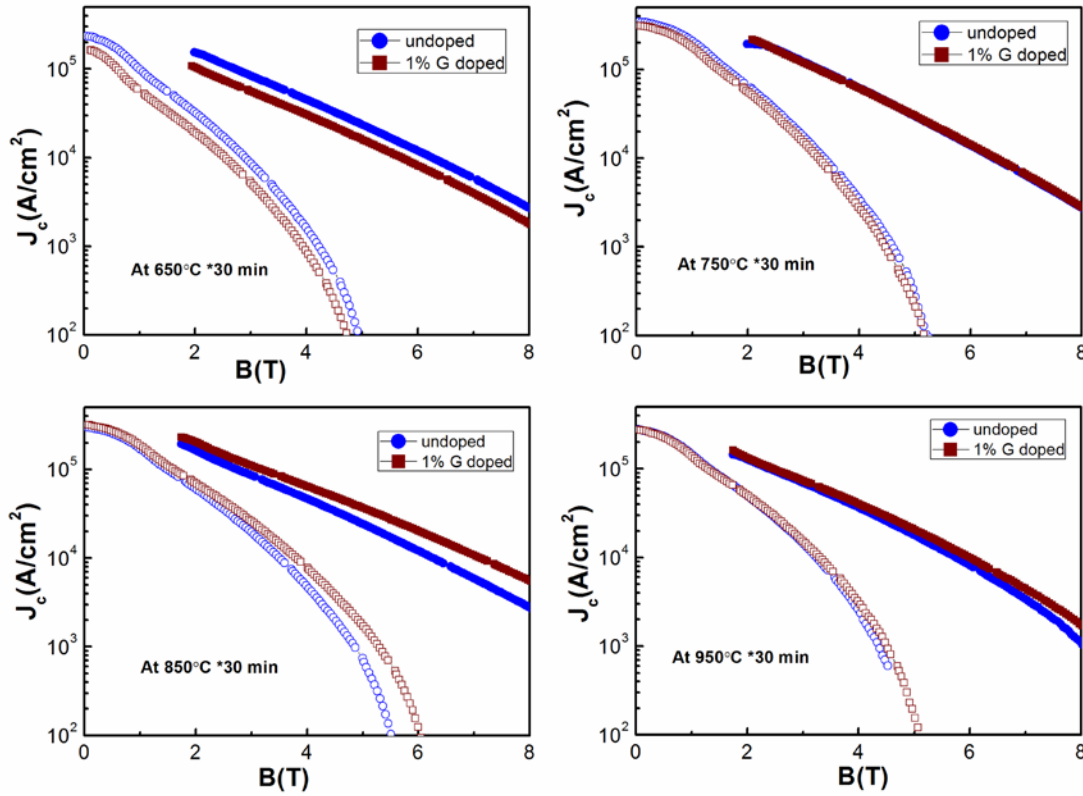


Fig. 2. In-field  $J_c$  performance of un-doped, and G-doped  $MgB_2$  bulk samples sintered at different sintering temperatures. Open symbols represent the data at 20 K while solid symbols represent the data at 5 K respectively.

temperatures improve the crystallinity, and hence the  $T_c$ . The G-doped samples too show the same trend with a slight reduction compared to the relevant un-doped sample. The normal state resistivity ( $\rho_{300K}$ ), shows a decreasing trend with increasing sintering temperature, revealing the increased grain perfection, which reduces the scattering due to disorder [13]. The residual resistivity ratio (RRR) also shows a similar trend, which gives evidence for the greater crystalline perfection produced by higher sintering temperatures [14]. The active cross-sectional area ( $A_F$ ), is improved slightly in the G-doped samples compared to the un-doped ones. At each sintering temperature, however, the improvement is as not remarkable as in samples made by the diffusion method [7]. This may be due to the short sintering time, which has an adverse effect on the crystallinity, and the low heat energy available to break the stable graphene structure, which therefore reduces the benefits of doping. On the other hand, reduction of  $A_F$  was observed for both samples sintered at 950 °C. The evaporation of Mg at high temperature may have played a dominant role over the improved crystallinity in this scenario [13].

The variation of the critical current densities ( $J_c$ ) with the applied field for the un-doped and G-doped  $MgB_2$  bulk samples prepared at different sintering temperatures is shown in Fig. 2. It can be clearly seen that the sintering temperature of the doped samples sintered at 650 °C is not sufficient to give any benefit from the doping with graphene. On increasing the temperature, however, a significant improvement in  $J_c$  performance can be seen due to doping, especially for the

sample sintered at 850 °C. Generally, crystalline boron is less reactive compared to amorphous boron, and therefore a high sintering temperature is needed for complete formation of  $MgB_2$ . This is the reason for the poor  $J_c$  performance observed for the samples sintered at low temperatures. The grain growth and improved crystallinity that occur at high temperatures also adversely affect the  $J_c$  performance, particularly at high field [13]. It is surprising to note that at the doping level of 1 at %, the sample sintered at 850 °C shows a  $J_c$  of  $5.6 \times 10^3$  A/cm<sup>2</sup> at 8 T, 5 K, which is nearly 2 times higher than that of the comparable un-doped sample, with a slight reduction  $T_c$  of 0.5 K. The results reveal that the most suitable sintering temperature for the in-situ method with the current precursors, is as high as 850 °C. 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  $J_c$  [15]. This, together with the improved connectivity, explains why the highest  $J_c$  performance is observed in the G-doped  $MgB_2$  sample that was sintered at 850 °C. It should be noted that the Bean's model, which used to calculate all the  $J_c$  results in this manuscript, did not distinguish the contribution of the local current in the superconducting clusters and the global critical current passing through the whole of the samples. However, the magnetic  $J_c$  can still be used for qualitative comparisons of the deference of  $J_c$  for  $MgB_2$  samples under high magnetic fields when the local current contribution was faded away [16].

The temperature dependence of the upper critical ( $H_{c2}$ ) and irreversibility ( $H_{irr}$ ) fields of the samples sintered at 750 °C and

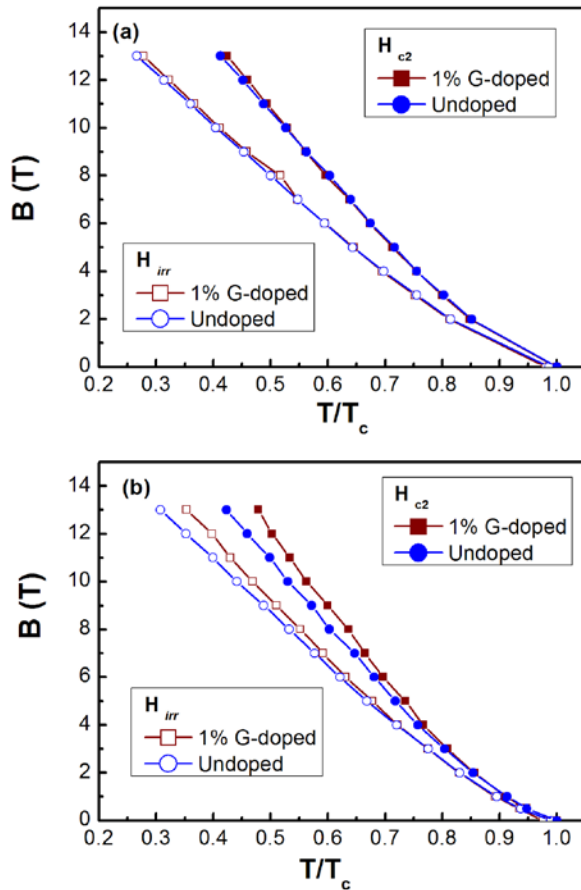


Fig. 3. Normalized temperature dependence of upper critical field  $H_{c2}$  and irreversibility field,  $H_{irr}$  for un-doped, and G-doped  $MgB_2$  bulk samples sintered at 750 °C (a) and 850 °C (b).

850 °C are shown in Fig. 3. It reveals that both  $H_{c2}$  and  $H_{irr}$  have increased due to doping compared to the un-doped sample sintered at 850 °C.  $H_{c2}$  and  $H_{irr}$ , however, remain the same for both the un-doped and the G-doped samples sintered at 750 °C. This gives evidence that effective carbon substitution has occurred under the sintering conditions at 850 °C. It is well-known that more scattering due to doping shortens the mean free path, thereby resulting in increased  $H_{c2}$ . Improved  $H_{c2}$  and  $H_{irr}$  due to doping were also observed in samples sintered at 950 °C, although the improvement of  $H_{c2}$  and  $H_{irr}$  at 850 °C is superior. This is due to the obvious grain growth and improved crystallinity that occurred at the higher sintering temperature, compared to sintering at 850 °C. Degradation of the crystallinity is directly linked to lattice disorder, which leads to improved high field  $J_c$  performance.

#### IV. CONCLUSION

A significant enhancement of critical current density under high magnetic fields was observed in G-doped samples sintered at 850 °C, without much reduction of  $T_c$ , which is due to effective carbon substitution, improved flux pinning and improved grain to grain connectivity. The improvement of  $J_c$  performance in the G-doped samples sintered at 850 °C is reflected by the improved  $H_{c2}$  and  $H_{irr}$ . We found that a considerably high temperature is needed to optimize the effects of G-doping on improving the  $J_c$  performance of  $MgB_2$  bulk

samples prepared through the in-situ method, using crystalline boron and graphene as precursors.

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