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Processing and characterization of graphene / graphene oxide doped MgB2 superconductors

Kaludewa Sujeewa De Silva

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Processing and characterization of graphene / graphene oxide doped MgB$_2$ superconductors.

Kaludewa Sujeewa Buddhimali De Silva

This thesis is presented as part of the requirement for the Award of the Degree of Doctor of Philosophy of the University of Wollongong

October 2012
Declaration

I, Kaludewa Sujeewa Buddhimali De Silva, declare that this thesis, submitted in partial fulfillment of the requirements for the award of Doctor of Philosophy, in the Institute for Superconducting & Electronic Materials (ISEM), Faculty of Engineering, University of Wollongong, Australia, is wholly my own work unless otherwise referenced or acknowledged. This document has not been submitted for a qualification at any other academic institution.

Kaludewa Sujeewa Buddhimali De Silva
October, 2012
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Abstract:

The discovery of superconductivity in MgB$_2$ has attracted enormous interest among the superconducting materials community. MgB$_2$ has emerged as a potential candidate for many applications, replacing conventional low critical temperature ($T_c$) superconductors, not only due to its high $T_c$ of $39$ K, but also to its intrinsically “weak-link” free grain boundaries, its rich multiple-band structure, and its low fabrication cost. Its rapid drop in critical current density ($J_c$) under applied magnetic field, and low upper critical field ($H_{c2}$), however, exclude it from many industrial applications where a high $J_c$ under high magnetic field is required.

Chemical doping can be identified as the simplest and cheapest way to improve the electronic structures of superconductors and their superconducting properties. Various types of carbon sources have been used as dopants for MgB$_2$ so far, and $J_c$ and $H_{c2}$ have been significantly enhanced due to charge carrier scattering, thanks to the two-band nature of MgB$_2$. The carbon doping, however, comes with its own drawback of reducing $T_c$, which limits the application temperature of MgB$_2$. Furthermore, many carbon dopants are detrimental to the performance of the low field $J_c$.

Therefore, the objective of the this work is to improve the critical current density of MgB$_2$ superconductor through chemical doping using graphene (G) and graphene oxide (GO) as the carbon sources, while addressing the common disadvantages of carbon doping. The work in this thesis is focussed on the processing and characterization of G- and GO- doped MgB$_2$ with the main objective being the enhancement of the critical current density at both low and high magnetic field. Therefore, the effects of G- and GO- doping in MgB$_2$ on the electromagnetic properties, as well as on the microstructural changes were studied systematically.
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. The effects of graphene doping on the superconducting properties of MgB$_2$ were studied using bulk samples made by the diffusion method. MgB$_2$ was chemically doped with graphene according to the formula MgB$_{2-x}$C$_x$, where $x = 0, 1, 3,$ and $5$ mol $\%$ graphene. It has been found that a small amount of graphene can significantly improve the $J_c$ and the intergrain connectivity, with only a small depression in the $T_c$. The optimally doped sample ($x = 1\%$), showed a $J_c$ that was 43 times higher compared to the undoped sample at 5 K, 8 T, with a drop in $T_c$ of slightly less than 1 K, together with an enhancement in the zero-field performance of $J_c$. This is a significant improvement as most carbon sources adversely affect the $J_c$ performance at low field. Low resistivity and comparatively improved critical fields were observed for the optimally doped sample. The improvement in grain-to-grain connectivity has been identified as one of the major factors responsible for such enhancement of the superconducting properties, especially for the low field performance of $J_c$. Characterization of the samples revealed improved intergrain connectivity and induced strain due to doping, while a noticeable increase in the flux-flow activation energy in graphene doped MgB$_2$ samples was observed at low fields. Furthermore, it was found that spatial fluctuation in the transition temperature ($\delta T_c$ pinning) is the flux pinning mechanism in graphene doped MgB$_2$, although this is uncommon for carbon doped MgB$_2$ samples.

Inspired by the improvements gained due to graphene doping, the effects of the chemical synthesis on the quality of the end product were investigated, along with the effects of doping the different end products into MgB$_2$. There have been different
procedures reported for the reduction of graphene oxide (GO), including chemical reduction, thermal annealing, and microwave irradiation. The presence of oxygen is inevitable in graphene synthesis. The carbon to oxygen ratio of the end product, however, totally depends on the method of preparation and the degree of the reduction process. Therefore, the effectiveness of a two-stage reduction process on reducing GO and the effects of these carbon additives on improving the superconducting properties of MgB₂ were systematically studied.

Reduced graphene oxide (rGO) and highly reduced chemically converted graphene (rCCG) samples were prepared under different processing conditions and were doped into MgB₂ by a diffusion process at 800 ºC for 10 hours. Both graphene types showed positive effects on the superconducting properties of MgB₂, however, addition of the rCCG type showed better improvement compared to the rGO addition. This is owing to the effective reduction that occurred during its synthesis process, which is evidenced by the X-ray photoelectron spectroscopy (XPS) analysis. rCCG addition had a considerable effect on the intergrain connectivity of MgB₂ samples, with positive consequences for the superconducting properties. Doping of MgB₂ with 1 mol% rCCG resulted in nearly 32% improvement of Jₖ at 5 K, 6 T over that of the rGO sample.

Although there is a improvement in the performance of Jₖ at high magnetic field in the graphene doped samples, it is not that pronounced compared to the performances of the other reported carbon sources such as SiC, carbon nanotubes (CNTs) or malic acid. Those dopants, however, always come with their own disadvantages in terms of degradation of the Jₖ in zero field.

Although SiC remains one of the best dopants, similar to any other carbon source, this too displays degradation of the critical current density (Jₖ) in low field. On the other hand, graphene has been recognized as a new dopant for MgB₂ which can improve the
zero field $J_c$ through improving the intergrain connectivity. Therefore, both graphene and SiC were used as co-dopants to investigate possible improvements in the superconducting performance of MgB$_2$. The superconducting properties characterized by $J_c$, intergrain connectivity, and critical fields were significantly improved due to co-doping.

The sample co-doped with graphene and 5 wt. % SiC showed improvements of 15% and 40% of $J_c$ at 20 K and zero field, compared to the 5 wt. % SiC doped and undoped samples respectively. Low resistivity and an apparent improvement in intergrain connectivity characterized the sample with both 5 wt. % SiC and graphene. This finding indicates that co-doping of MgB$_2$ in the way described can result in complementary beneficial effects on the superconducting properties.

Although significant property enhancement can be attained through graphene doping, the high cost involved in its synthesis renders the use of graphene impractical in large-scale applications. On top of that, restacking of graphene sheets during the synthesis process results in an inevitable reduction of the MgB$_2$ performance in applications. On the other hand, GO, which is typically monolayer in nature, can be used as a dopant and it has the advantage of thermal reduction into mono layers of graphene during the MgB$_2$ sintering process, which prevents the aggregation of graphene sheets in the matrix. In addition to that, the high possibility of attaining homogeneous dispersions of GO in organic solvent would result in good dispersion of the dopant in the matrix, which would improve the effectiveness of the dopant even more.

Based on above considerations, the effects of graphene oxide (GO) doping on the superconducting properties of MgB$_2$ were studied using bulk samples made by the diffusion method. Homogeneous dispersions of GO in tetrahydrofuran (THF) were obtained through a novel synthesis method. MgB$_2$ was then chemically doped according
to the formula MgB\textsubscript{2-x}C\textsubscript{x}, where x = 0, 1, 2, 3, and 4 at\% GO in THF. It was found that GO doping significantly improves the critical current density, both at low and at high magnetic fields, which distinguishes GO from all the other elements doped into MgB\textsubscript{2} so far. This type of doping results in significant improvements in grain-to-grain connectivity, and to the irreversibility and upper critical fields of MgB\textsubscript{2}, with only a small depression in the superconducting transition temperature. Furthermore, a noticeable increase in the flux-flow activation energy in graphene doped MgB\textsubscript{2} samples was also observed. Microstructural investigations revealed the improved intergrain connectivity and induced strain due to doping.

The sample with 2 at\% GO showed a $J_c$ that was 27 times higher compared to the undoped sample at 5 K, 8 T, with a slight drop in $T_c$ of just 1.2 K. At the same time, this doping level resulted in a 50% enhancement of the $J_c$ performance at 20 K at zero field, over that of the undoped sample. This improved $J_c$ performance at both zero field and high field can be attributed to the improved intergrain connectivity and increased $H_{c2}$, respectively.

Overall, the work presented in this thesis is mainly based on the processing and characterization of graphene, graphene oxide, and bulk MgB\textsubscript{2} samples. These results are important for future MgB\textsubscript{2} fabrication.
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Alternating current $ac$
Boltzmann’s constant $k_B$
Carrier density $n_s$
Coherence length $\xi$
Critical current density $J_c$
Critical transition temperature $T_c$
Density of states $DOS$
Energy gap $\Delta$
Field emission scanning electron microscope $FESEM$
Flux pinning force $F_p$
Full width at half maximum $FWHM$
High resolution electron microscopy $HREM$
High temperature superconductor $HTS$
Hot isostatic pressing $HIP$
Irreversibility field $H_{irr}$
Lower critical field $H_{c1}$
Low temperature superconductor $LTS$
Penetration depth $\lambda$
Phonon density of states $PDOS$
Physical properties measurement system $PPMS$
Powder-in-tube $PIT$
Resistivity near $T_c$ $\rho_0$
Residual resistivity ratio $RRR$
<table>
<thead>
<tr>
<th>Term</th>
<th>Abbreviation</th>
</tr>
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<tbody>
<tr>
<td>Scanning electron microscopy</td>
<td>SEM</td>
</tr>
<tr>
<td>Transmission electron microscopy</td>
<td>TEM</td>
</tr>
<tr>
<td>Upper critical field</td>
<td>H$_{c2}$</td>
</tr>
<tr>
<td>X-ray diffraction</td>
<td>XRD</td>
</tr>
<tr>
<td>X-ray photoemission spectroscopy</td>
<td>XPS</td>
</tr>
</tbody>
</table>
Chapter 1: Introduction

1.1 History of superconductivity

Superconductivity is the name given to a remarkable combination of electromagnetic properties which appear in certain materials when they are cooled to extremely low temperatures. Superconductors are materials that lose their resistance to electrical current flow below a certain critical temperature ($T_c$), a certain critical current density ($J_c$), and a certain critical field ($H_c$). Many materials become superconducting when they are cooled to near absolute zero temperature (-273°C).

Superconductivity was discovered in 1911 by H. Kamerling Onnes when he had first liquefied helium. He was able to reduce the temperature of liquid helium down to as low as 0.9 K and began to investigate the electrical properties of metals at extremely low temperatures. He found that the electrical resistivity of mercury was suddenly dropped to zero (a lower than measurable value) when the sample was cooled below 4.2 K [1]. He realized this phenomenon represented a new physical state and named it the “superconducting state”. Later, in 1913, he won a Nobel Prize in Physics for his research in this area.

The next great milestone in understanding how matter behaves at extremely cold temperatures occurred in 1933. The German researchers Walther Meissner and Robert Ochsenfeld discovered that a superconducting material not only possesses zero resistance, but also repels a magnetic field. This phenomenon is known as the “Meissner effect” [2]. The Meissner effect is so strong that a magnet can actually be levitated over a superconducting material.
In 1986, higher $T_c$, above 35 K was observed in the Ba-La-Cu-O system [3]. Following this, Tl-Ba-Cu-O was found to exhibit $T_c$ of 125 K [4]. Later on, Hg-Ba-Ca-Cu-O was shown to be superconducting at 134 K [5]. Up to now, the record for the highest superconducting temperature is still held by the Hg-based superconductor which was found in 1993.

In 2001, Nagamtsu and his group found a simple binary compound of magnesium and boron, magnesium diboride (MgB$_2$), to be an extraordinary new superconductor which shows a $T_c$ of 39 K, far above the highest $T_c$ of any of the elemental or binary alloy superconductors [6]. Laboratory testing has found that the performance of MgB$_2$ will surpass those of NbTi and Nb$_3$Sn wires in high magnetic field applications such as high field magnets [7].

In 2008, an iron-based family of high temperature superconductors was discovered, starting with lanthanum oxygen fluorine iron arsenide (LaO$_{1-x}$F$_x$FeAs) with $T_c$ of 26 K [8]. Further research work on this family, replacing lanthanum with other elements such as samarium and neodymium, has identified compounds with higher and higher $T_c$, such as 52 K [9, 10]. In 2009, a new member (BaFe$_{1.9}$Pt$_{0.1}$As$_2$) in the family of superconducting FeAs-based materials was found to show superconductivity near 23 K [11]. Later in the year, BaFe$_2$As$_2$ was reported, with increased $T_c$ up to 35 K, using a high pressure synthesis method [12].

The puzzling phenomenon of superconductivity was explained by the Bardeen Cooper Schrieffer (BCS) theory in 1957. Here the first widely-accepted theoretical understanding of superconductivity was put forward by American physicists John Bardeen, Leon Cooper, and John Schrieffer. Their theory of Superconductivity became known as the BCS theory – which the letters standing for the first letter of each person's
last name. This contribution was honoured with a Nobel Prize in 1972. According to the theory, the electrical transport in superconductors is due to the pairing of electrons (Cooper pairs) with opposite moment and spins instead of single electrons. The coherent travelling of electron pairs leads to resistance-less current flow through a superconducting material [13].

The Josephson effect, which is another significant theoretical advancement, came in 1962, when Brian D. Josephson, a graduate student at Cambridge University, predicted that electrical current would flow between two superconducting materials - even when they are separated by a non-superconductor or insulator [13]. This tunnelling phenomenon was later confirmed and this led him to win the Nobel Prize in Physics in 1973.

1.2 Fundamentals of superconductivity

There are three important parameters often used to characterize the performance of a superconductor, the critical temperature, $T_c$, the critical field, $H_{c2}$, and the critical current density, $J_c$. Superconductors are the materials that show zero resistance to the flow of electricity and ideal diamagnetism below a certain temperature. This temperature is called the superconducting transition temperature or critical temperature ($T_c$). As shown in Figure1.1, with increasing temperature above $T_c$, the resistivity regained again, and the material return to the normal state.

The critical temperature is inherent to the material, although impurities in it can vary this a bit. On cooling, the transition from the normal state to the superconducting state occurs very sharply when the materials is pure and physically perfect, where as a broadened transition represents an impure or less perfect crystal structure [13]. A
superconductor shows perfect diamagnetism when is cooled below $T_c$. This phenomenon is known as the Meissner Effect [13].

The maximum current that a superconductor can carry in the superconducting state is called the critical current ($I_c$). When this is expressed in terms of current per unit area, it is called the critical current density, $J_c$. Above this value, the superconductivity is destroyed and the material returns to the normal state.

The critical current density can be affected by several intrinsic and extrinsic parameters, which will be discussed further in the Chapter 2. The application of a magnetic field higher than a certain value can also destroy the superconducting state. This threshold value, $H_{c1}$, is called the critical magnetic field [13, 14].

This value depends on the temperature, following a parabolic law according to Equation (1.1) given below.

$$H_c = H_0 \left[1-(t/T_c)^2\right]$$  \hspace{1cm} (1.1)

Where, $H_0$ - critical field at absolute zero

$T_c$ - transition temperature

Figure 1.1: Temperature dependence of the resistivity in superconductors
These three important parameters, i.e., $J_c$, $T_c$, and $H_c$ determine the state of the material, and therefore, they are called the critical parameters of the superconductor. The relationship among these parameters is elaborated in Figure 1.2 [14].

According to the Meissner effect, a metal in the superconducting state never allows any magnetic flux density to exist in its interior, instead, it will create a shielding current so as to cancel the applied magnetic field [2, 13, 14]. The difference between a superconductor and a perfect conductor is that the superconductor expels all magnetic fields when it goes through the superconducting transition.

![Figure 1.2: $J_c$, $T_c$, and $H_c$ phase diagram showing the relationship between the three critical parameters of a superconductor [14].](image)

Superconductors can be divided into two classes, type-I and type-II, according to their response to magnetic field. Most of those pure elements which are superconductors exhibit type-I superconductivity, whereas alloys generally exhibit type-II superconductivity [13, 14].

When a type I superconductor is placed in a weak external magnetic field, the field penetrates the superconductor for only a short distance, called the London penetration
depth ($\lambda_L$), over which it decays to zero, according to Equation (1.2) given below [13, 14].

$$B(x) = B(0) \exp(-x/\lambda_L)$$  \hspace{1cm} (1.2)

Where, $B(0)$ - the flux density of the applied fields at the surface
$x$ - the distance from the surface

There was a discrepancy, however, between the experimentally observed penetration depth, $\lambda$, and the London penetration depth, $\lambda_L$, which was corrected by using the coherence length, $\xi$, and mean free path, $l$, according to the Eq. (1.3) [15]. The coherence length, $\xi$, is regarded as the distance between the surface and where the sample reaches the density of superconducting electrons $n_s$, which is of the order of $10^{-4}$ cm for a pure superconductor [13]. Here, $\xi$ is treated as analogous to $l$ and dependent on the purity of the material.

$$1/\xi = 1/\xi_0 + 1/l$$  \hspace{1cm} (1.3)

Where, $\xi_0$ is the coherence length for a perfectly pure superconductor.

When the material is impure, the coherence length is reduced [13, 16]. Thus the coherence length of an impure material is given by $\kappa = \lambda / \xi$, where $\kappa$ is the Ginzburg-Laudau (GL) parameter. If the superconductor contains some impurities, this means a higher normal state resistivity as a result of the scattering of electrons which shortens the coherence length $\xi$ and leads to higher $\kappa$ value [13].

According to the well known BCS theory, an energy gap between the ground state and the quasi-particle state exists for superconducting materials, which has a width $\Delta$ equals to $1.76 k_B T_c$, where $k_B$ is Boltzmann’s constant (see Figure 1.3). For normal metals at absolute zero, however, all energy states are filled up to Fermi energy, $E_F$ [13].
The main concept of this theory is to introduce the so-called Cooper pairs, the charge carriers of the superconducting state, which tends to have lower energy levels due to the attractive interactions between electrons near the Fermi energy. These Cooper pairs are then split up into two quasi-particles by thermal agitation when the temperature is raised above absolute zero, which tends to decrease the energy gap, so that at $T_c$, it will become zero [13, 16].

According to Abrikosov’s investigations, there is an exact value of the GL parameter, $\kappa$, at which the superconductors can be categorized into two types. When $\kappa < 1/\sqrt{2}$, the superconductor falls into type I, while if $\kappa > 1/\sqrt{2}$ the superconductor falls into type II [16].

In type II superconductors, the field penetrates in the same way as in type I, up to the first critical field $H_{c1}$. Raising the applied field above $H_{c1}$ leads to a mixed state (or Shubnikov state) in which magnetic field additionally penetrates the superconductor in the form of thin filaments. These filaments are called magnetic vortices, and each of them carries one magnetic flux quantum ($\Phi_0 = 2.067 \times 10^{-15} \text{Tm}^2$) [14]. On increasing field further above $H_{c1}$, an increasing amount of magnetic vortices penetrates the
material, but there remains no resistance to the flow of electrical current, as long as the magnetic vortices do not move under the influence of the electrical current and magnetic field. These flux lines consist of normal cores which are surrounded by a vortex of supercurrent, which decays over a distance of $\lambda(T)$ for bulk samples. The diameter of the vortices is of the order of the coherence length of the superconductor, $\xi$, i.e. typically nanometers (coherence length of MgB$_2$ $\approx \xi_{ab}(0) = 3.7$–$12.8$ nm, $\xi_c(0) = 1.6$–$5.0$ nm) [17]. As shown in Figure 1.5, at the upper critical field $H_{c2}$, superconductivity is destroyed and the material becomes to its normal state [13, 14, 17]. When an external current density, $J$, is applied to a type II superconductor perpendicular to the direction of applied magnetic field, these flux lines tends to move under the influence of the Lorentz force, $F_L$, as shown in Figure 1.5. There will be a Lorentz force acting on each vortex, at right angles to both the direction of the transport current and to the direction of the flux.

Figure 1.4: Phase diagrams of type-I and type-II superconductors

Since vortex movement results in resistivity, it is very important to obstruct this motion, in order to keep the material at the superconducting state. Magnetic vortices can be
effectively pinned at sites of atomic defects, such as dislocations, stacking faults, inclusions, impurities, and grain boundaries. The defects are the most effective pinning centres when their size roughly matches the size of the vortices. Therefore, the performance of superconductors is greatly affected by the effectiveness of vortex pinning and hence by the type, density, and extent of these defects [13].

Another important parameter for superconductors is $H_{irr}$, which is very important in determining the upper limit of the magnetic field for practical applications. This is the de-pinning field, where the vortex pinning or critical current is immeasurably small. This value gives an idea about the pinning properties of the superconductor. If the difference between $H_{c2}$ and $H_{irr}$ is small, the material shows good pinning properties [13, 18].
1.3 Applications of superconductors

Today, superconducting materials have a wide range of commercial and industrial applications in energy production, storage, and distribution, in sensor materials, and in high field magnets. The low-temperature superconductors (LTS), particularly NbTi ($T_c$ of 9 K) and Nb$_3$Sn ($T_c$ of 18 K) are currently used in magnetic resonance imaging (MRI), nuclear magnetic resonance (NMR), and magnets for plasma fusion devices [7]. Nb-47wt. %Ti alloy has emerged as the main commercial superconductor because it can be economically manufactured in a ductile form with a nano-structure that is very suitable for high critical current. The use of Nb$_3$Sn based strands is also prominent due to their capability of being manufactured into strong composites in km lengths and their microstructures that promote high critical current densities [7].

The high-temperature superconductors (HTS), particularly bismuth strontium calcium copper oxide (BSCCO) (Bi-2223, $T_c$ of 110 K, and Bi-2212, $T_c$ of 85 K) and YBa$_2$Cu$_3$O$_{7-x}$ (YBCO, $T_c$ of 92 K) are currently used in electric power applications [4, 7]. Electric generators made from superconducting wire are another fabulous invention as they improved the efficiency compared to conventional generators wound with copper wire. In fact, their efficiency is above 99%, and their size is about half that of conventional generators.

Recently, power utilities have also begun to use superconductor-based transformers and "fault limiters" with tremendously improved performance. The Swiss-Swedish company ABB was the first to connect a superconducting transformer to a utility power network in March 1997. ABB also recently announced the development of a 6.4 MVA fault current limiter - the most powerful in the world [19].
The main use of superconductors in the electronics industry is in ultra-high-performance filters where the near zero resistance of the superconducting wire plays a great role. This translates into an ability to pass desired frequencies and block undesirable frequencies in high-congestion radio frequency applications such as cellular telephone systems. Superconductors have also found widespread applications in the military. HTSC superconducting quantum interference devices (SQUIDS) are being used by the U.S. Navy to detect mines and submarines. Uses of superconductors in X-ray detectors, and ultra-fast light detectors can be considered as emerging technologies [19].

Magnetic-levitation (MAGLEV) is an application where transport vehicles such as trains can be made to "float" on strong superconducting magnets. This eliminates friction between the train and the track. The first commercial use of MAGLEV technology occurred in 1990, when it gained the status of a nationally-funded project in Japan [19].

1.4 Potential of MgB$_2$ for superconducting applications

MgB$_2$ is a promising superconductor for high magnetic field applications at temperatures near 20 K. The applications of MgB$_2$ are strongly dependent on the development of the cryocooler. The cryogenic refrigeration system that is required for operating at temperatures near 20 K is much less complex and more energy saving compared to those operate at temperatures of near 4 K. For example, today's MRI machines are made using niobium-alloy wires, which are quite expensive. Furthermore, they require liquid helium refrigeration to maintain their superconducting properties, which is also costly in an ongoing way. If the performance of MgB$_2$ can be improved, it
can be used to replace the expensive niobium-alloy wires, which will reduce the cost of the equipment, and the higher $T_c$ of MgB$_2$ is also beneficial from reducing the cost of maintaining the refrigeration. Hyper Tech Research (HTR) in the US, Columbus Superconductors in Italy, and Hitachi Ltd in Japan, have constructed numerous demonstration coils and magnets. Columbus Superconductors and ASG Superconductors, constructed the first demonstration of an open MRI system incorporating 12 pancake shaped MgB$_2$ coils, each wound with 1.8 km of wire. The MRI reached a central magnetic field of 1.0 T at an operating temperature of 16 K, produced cryogen-free open MRI systems.

An FCL (fault current limiter) is a device used in electrical power transmission and distribution systems. The uses of FCLs provides a significant advantage in avoiding the enormous costs associated with upgrading existing power systems to cope with the continual increase in fault current levels. Investigation of the usability MgB$_2$ for the FCL applications will be beneficial due to its low manufacturing costs, the ability to form into long length wires, and high critical current capacity under economic cryogenic operational temperature. The usability of MgB$_2$ in high magnetic field applications is still under investigation, however, based on the preliminary laboratory testing, it seems that, MgB$_2$ will be a strong competitor for Nb-based superconductors in high magnetic field applications [7].

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 for its use in both large-scale applications and electronic devices. Especially, from the economic point of view, the costs of the raw materials for both Mg and B will be several times less than for the ones used for Nb-based superconductors.
The critical current density of pristine MgB$_2$ drops rapidly in the high magnetic field, however, due to the weak pinning centres and low upper critical field. Extensive research has been carried out with the aim of improving the usability of MgB$_2$, by methods including chemical doping, irradiation, and thermo-mechanical processing techniques [20-31]. Chemical doping is known to be the simplest way to improve the superconducting properties of MgB$_2$ superconductors. Among the many dopants investigated, carbon dopants are at the forefront, due to their capacity for addressing the drawbacks to MgB$_2$, particularly in terms of improving the performance of $J_c$ at high fields and improving the $H_{c2}$ [18, 20-22, 24, 25, 32-38]. Rapid developments in the processing of MgB$_2$ in the forms of single crystals, bulk samples, tapes, wires, and thin films hold promise for the realization of practical applications in the near future.

1.5 Aim and outline of the thesis

Extensive research has been undertaken to investigate the possibilities of improving the practical usability of MgB$_2$, however, there is still more room for improvement, particularly in, improving the performance of $J_c$ both at low and high magnetic fields, together with obtaining better $H_{c2}$ at the same time. The main objective of this research is to improve the superconducting performance of MgB$_2$ both at low and high magnetic fields together with achieving better $H_{c2}$ via chemical doping, using graphene and graphene oxide as the carbon source.
The outline of the thesis is as follows:

1. Chapter 1 reviews the history, and fundamentals of the superconductivity, applications of superconductors, and the potential of MgB$_2$ for superconducting applications.

2. Chapter 2 presents a detailed literature review on MgB$_2$ superconductor, including the crystal electronic structure, the superconducting performance in terms of $T_c$, $J_c$, $H_{c2}$, and $H_{irr}$, and the effects of doping and preparation methods on MgB$_2$.

3. Chapter 3 reports on the equipment and the experimental procedures used in this thesis.

4. Chapter 4 investigates the effects of graphene doping on improving the superconducting properties of MgB$_2$.

5. Chapter 5 investigates the effects on the reduction process during synthesis of graphene on improving the superconducting properties of MgB$_2$.

6. Chapter 6 investigates the effects of co-doping with graphene and SiC on improving the superconducting properties of MgB$_2$.

7. Chapter 7 investigates a novel method for producing a homogeneous dispersion of GO and its doping effects to improve the superconducting properties of MgB$_2$.

8. Chapter 8 contains the conclusions and suggestions for further improvements.
1.6 References


Chapter 2: Literature Review on Magnesium Diboride (MgB₂)

2.1 Introduction

The discovery of superconductivity in MgB₂ at 39 K has attracted great interest around the world, since the critical temperature of MgB₂ is the highest among the inter-metallic superconductors [1]. Although high temperature superconductors are available, practical applications of MgB₂ are significant, as it is cheaper. Unlike cuprates, MgB₂ has a lower anisotropy, larger coherence lengths, and transparency of the grain boundaries to current flow, which makes it a significant superconductor. Furthermore, MgB₂ promises a higher operating temperature and a higher device speed than the present electronics based on Nb [2]. In addition, the ease of fabrication in different forms such as bulk, wire, tape and thin film, is another fascinating feature of MgB₂ that supports its potential as the emerging superconductor for the next generation superconductor applications.

To make MgB₂ really viable, however, the critical current density (Jc) of MgB₂ superconductor must be raised considerably. Considering all the above, MgB₂ has emerged as a good candidate for many of the superconducting applications, yet needs to be developed further to enhance its superconducting properties as to achieve the desired properties to suit each application.

2.2 Crystal structure and two gap conductivity

The unit cell of MgB₂ possesses a simple hexagonal AlB₂-type structure (space group P6/mmm), which is common among borides. The MgB₂ crystal structure is shown in
Figure 2.1[2]. It contains graphite-type boron layers, which are separated by hexagonal close-packed layers of magnesium. The lattice parameters are, $a = 3.086$ Å (equal to the in-plane Mg-Mg distance), and $c = 3.524$ Å (the distance between Mg- layers). These values of lattice parameters for MgB$_2$ are sitting in the middle of the values of lattice parameters for the other AlB$_2$-type compounds. The magnesium atoms are located at the centre of hexagons formed by boron atoms and donate their electrons to the boron planes. It seems that Mg is fully ionized in this compound. The electrons donated to the system, however, are not localized on the anions, but are spread over the whole lattice [3]. Similar to graphite, MgB$_2$ exhibits a strong anisotropy in the B-B lengths: the distance between the boron planes is significantly longer than in-plane the B-B distance [4-6]. There is no sign of a structural transition for MgB$_2$ down to 2 K or under high pressure of 40 GPa [2].

MgB$_2$ is the first to fall onto the special group of multi-gap superconductors which was predicted 50 years ago. This multi-gap nature has been proven by several experimental studies, including studies based on heat capacity, Raman scattering, point contacts, and optical and magnetic properties of polycrystalline samples or single crystals [7-14].

Figure 2.1: The crystal structure of MgB$_2$ superconductors
The $sp^2$ boron orbitals overlap, creating $\sigma$-bonds within the neighbouring atoms in the plane while the remaining $p$ orbitals extend above and below the plane and create $\pi$-bonds in MgB$_2$. One $\pi$-bond is conduction type, and the other is valence type. The other bonds are two dimensional $\sigma$-bonds formed by the covalent $p_{xy}$ boron orbitals: both types of $\sigma$-bonds are hole type [4, 5]. These bonds represent four discrete electron energy levels at the Fermi surface. The Fermi surface of MgB$_2$ is shown in Figure 2.2. Here, $\Gamma$, L, M, A are sites in Brillouin zone. The $\sigma$-bands form two hole-like coaxial cylinders along the $\Gamma$- A line, and the $\pi$-bands form two hole-like tubular networks near $K$ and M, and an electron-like tubular network near H and L [3]. The asymmetry of the charge distribution in the $\sigma$-bonding with respect to the in-plane boron atoms causes strong coupling of the $\sigma$-bonding state to the in-plane vibration of boron atoms, which is mainly responsible for the superconductivity in MgB$_2$ [5, 15]. Electrons at these different Fermi levels form pairs with different bonding energies. Each $\pi$-bond and $\sigma$-bond has particular energy gaps at the Fermi surface. The average values of the gap are 6.8 meV for $\sigma$-bonds and 1.8 meV for $\pi$-bonds.

![Image of Fermi surface of MgB2 superconductors](image)

Figure 2.2: The Fermi surface of MgB$_2$ superconductors with symmetry directions of Brillouin zone [4].
The evidence for two-gap superconductivity in MgB$_2$ was confirmed by experimental studies using several techniques, such as tunnelling spectroscopy, point contact tunnelling, specific heat capacity, etc. [9, 10, 16-21].

2.3 Fabrication methods

MgB$_2$ has been synthesized in various forms: bulk, thin films, powders, wires and tapes, as well as single crystals. MgB$_2$ can be synthesized by a simple route from the reaction of B with Mg vapour, generally at temperatures above 650 °C (which is the melting point of Mg). The binary diagram for Mg-B is shown in Figure 2.3.

Figure 2.3: The binary phase diagram for Mg-B [23].
The labels Solid, Liquid, and Gas represent the Mg-rich solid, liquid, and gas phases, respectively [22]. From the phase diagram, it is evident that there is a big variation of processing temperature from around 650 °C-1000 °C to form MgB₂ as the liquid phase of MgB₂ exists in this range at 1 atm.

2.3.1 MgB₂ bulk

Fabrication of bulk can be categorized into two main methods, called in-situ and ex-situ. In the in-situ method, a mixture of B and Mg powders is first formed into the desired shape (i.e, pellet, wire, or tape) which is followed by a suitable heat-treatment under inert atmosphere (usually Ar) [23]. In ex-situ, reacted powder is used to form the sample into the desired shape [5, 24, 25]. The main advantage of the ex-situ method over the in-situ method is the higher density of the final product, however, the main drawback of this is the poor grain connectivity [6, 26, 27]. In addition to the poor grain connectivity, the commercially reacted powder shows a broad range of particle sizes, which makes it difficult to control process parameters. Planetary ball milling of the precursor powder, however, helps to crush the powder, which leads to fine grains of MgB₂ and distributes the MgO inclusions more evenly, which both have positive effects on improving the connectivity and flux pinning, and hence the critical current density [28-30].

The in-situ method offers more benefits for MgB₂, such as better connectivity, relative ease in introducing doping, and better control over the stoichiometry, however, there is the problem of the low density of the final product, which causes dissipation of the current flowing through the product [31]. The grain connectivity of in-situ prepared MgB₂, however, is highly dependent on the size and the purity of the precursor powders.
[23, 28, 32]. The presence of MgO is inevitable in MgB$_2$, as it is introduced to the system through the precursors. The surface of Mg is easily oxidized in air, and boron usually contains B$_2$O$_3$ in small amounts. Both of these cause the formation of MgO, which is also favoured by its Gibbs free energy, so that the formation of MgO occurs easily than the formation of MgB$_2$ [33]. This greatly affects the inter-grain connectivity, and thereby also the critical current density [34]. According to Liao et al. [35], however, the presence of nanosize MgO is beneficial in increasing the effective flux pinning, and hence improving $J_c$.

Several techniques have been suggested by many groups to improve the density of MgB$_2$ based on using high pressure and high temperature [36-38]. The density of the in-situ product can be improved by using hot isostatic pressing (HIP) and high pressure synthesis [31, 36, 39-42]. Flukiger et al. [43] reported on a cold high pressure technique that can greatly enhance the $J_c$ due to improved density.

Mechanical alloying (MA) is another way of improving the superconducting properties of MgB$_2$. The high energy milling of precursor materials leads to fine grain structure of the end product with enhanced superconducting properties. Mechanically alloyed samples show grains about 1000 times smaller than HIP samples and samples sintered at high pressure [30, 44-47]. The observed improvement in $H_{irr}$ and high $J_c$ manifest improved flux pinning of MA samples, which is due to the small grains and the enhanced number of grain boundaries. The results gained for MgB$_2$ with carbon doping under high-energy mechanical milling showed huge enhancement of the critical current density and the upper critical field [44, 48].

Another way of fabricating of high dense MgB$_2$ is called the diffusion technique, where a bulk or wire sample is first prepared with B and then Mg is made to diffuse into it during synthesis. The process is rather simple, however, a long sintering time is needed...
to obtain better properties. This long sintering, on the other hand, offers the advantage of improved crystallinity. In contrast to the in-situ process, the boron pellet that is buried in the Mg source in this method offers the advantage of a highly dense product. The formation of MgO is very limited, due to the low MgO diffusivity. Therefore, this process offers a highly dense product with better $J_c$ performance as a result of a larger effective cross-sectional area [49, 50].

**2.3.2 MgB$_2$ tapes and wires**

For practical applications, long-length conductors are required in the form of tapes and wires. The general fabrication techniques for wire and tape fabrication are the powder-in-tube (PIT) process and continuous tube forming and filling (CTFF). PIT involves filling metallic tubes with powder, followed by drawing and rolling the filled tubes into wires and tapes, as shown in Figure 2.4 [51]. Unlike the low $T_c$ superconductors, NbTi and Nb$_3$Sn superconductors, MgB$_2$ is not significantly affected by weak links and shows high transport critical current densities for tape and wire samples [43, 52-54]. In the in-situ PIT method, a mixture of Mg and B powders is used to fill the metallic tubes followed by subsequent deformation and heat treatment [26, 55]. The ex-situ PIT technique consists of direct filling of the metallic tubes with reacted MgB$_2$ powder, followed by deformation. Heat treatment at 600-1000 °C is usually applied to the cold-worked tape or wire to obtain superconductivity [2, 56]. Although the ex-situ fabrication process is cheaper and simpler, the in-situ process has the advantage of being able to improve the performance of $J_c$ by such means as chemical doping [27, 57].
The selection of the sheath material for the fabrication of MgB\textsubscript{2} wires and tapes is crucial. Generally, normal metal cladding provides parallel electrical conduction, thermal stabilization, and mechanical protection for the superconductor cores. The sheath material should be compatible with MgB\textsubscript{2} in order to preserve its superconducting characteristics and should possess enough hardness and ductility to undergo the essential mechanical deformation during the fabrication.

The usual sheath materials which have been applied to MgB\textsubscript{2} core are stainless Steel (SS) \cite{33, 51}, iron \cite{43, 57-63}, Cu \cite{56, 64, 65}, Ag \cite{65, 66}, Ni \cite{64, 67}, and Cu–Ni \cite{30, 68-70}. Considering the process conditions, however, iron has been found to be the best material for MgB\textsubscript{2} due to its ductility, low cost, and light weight, as well as its suitability for the fabrication process in large-scale industrial production \cite{71, 72}.

Figure 2.4: Schematic of the powder in tube (PIT) in-situ and ex-situ methods \cite{54}
In the CTFF process, powder is fed onto a strip of metal as it is being continuously formed into a tube. High purity long Fe strips are formed continuously into a tube with an overlap-closed tube process and the powder being enclosed in the sheath. After this, the closed tube can be inserted into a seamless tube and deformed to the round wire [5, 68]. A variation of the PIT preparation route is reactive liquid infiltration [73]. This technique has been used to fabricate both monofilamentary and multifilamentary wires several tens of meters in length. The process includes the cold-working of a composite billet. The process starts with a steel clad thin niobium (Nb) tube filled with a cylindrical magnesium rod and fine boron powder. The MgB₂ compound is formed inside the Nb tube upon heat treatment, resulting in a very compact, dense and finely grained MgB₂.

![Figure 2.5](image)

Figure 2.5: A comparison of transport $J_c$ in applied fields for MgB₂ conductors fabricated by different methods [80]. Data for the figure were taken from references given in the square brackets.
Similarly, Togano et al. [74] proposed an approach for the fabrication of MgB$_2$ tape by an interface diffusion reaction between a Fe–Mg alloy substrate and a boron layer. The Mg in the Fe–Mg alloy diffuses towards the interface during the heat treatment, forming a thin Mg-rich layer along the interface. Then, the Mg rich thin layer acts as a source of Mg for MgB$_2$ formation, which proceeds to the inside of the B layer. Single crystals are currently obtained by the solid–liquid reaction method from Mg-rich precursor, under high pressure in an Mg-B-N system and by the vapour transport method [75, 76].

Recently, Nishijima et al. [77], reported on a significant enhancement of the critical current density (nearly five times larger at 4.2 K at 5 T) and the transverse compressive stress tolerance of wires fabricated by the internal Mg diffusion process compared to the PIT process [77]. This improvement is attributed to improved connectivity and grain boundary pinning. This method is also an improved version of the diffusion process, first reported by Giunichi and co-workers [73]. Although this method offers high density and better connectivity, from a practical point of view, this method is currently only suitable for making short samples, however, the feasibility of fabrication of long-length wires needs to be tested. A comparison of transport J$_c$ in applied fields of MgB$_2$ conductors fabricated by different methods is shown in Figure 2.5 [2, 33, 54, 67, 73, 78-82].

### 2.4 Properties of MgB$_2$

The most important parameters in superconductors are the critical temperature (T$_c$), the critical current (I$_c$) or critical current density (J$_c$), upper critical field (H$_c2$), and the irreversibility field (H$_{irr}$). One of the most important applications of superconductors is in the area of high current and high fields, where superconductors with high J$_c$ are preferred. The critical current density (J$_c$) of pristine MgB$_2$, however, drops rapidly
with increasing magnetic field, which is mainly due to its poor pinning and low upper critical field, \( H_{c2} \). In order to get the benefit of the high \( T_c \) of MgB\(_2\), the above-mentioned parameters need to be enhanced. Several techniques can be used to optimize the superconducting properties of MgB\(_2\), such as chemical alloying, irradiation, and thermo-mechanical and magnetic shielding techniques.

### 2.4.1 Critical temperature

Critical temperature \((T_c)\) is one of the most important parameter which limits the working temperature of a superconducting application. The \( T_c \) of MgB\(_2\) is around 39 K (-234 °C), which is the highest among the inter-metallic superconductors [1]. The value of \( T_c \) greatly depends on the crystal structure, hence, any variation of the lattice parameters will affect \( T_c \) [83, 84]. Experimental results show the changes in the experimental conditions such as isostatic pressure [85-87] or neutron irradiation [88, 89] lead to change in the lattice volume, which is then responsible for reduced \( T_c \). Furthermore, Mg deficiency could leads to increased lattice strain, which results in reducing \( T_c \) [90]. Low crystallinity always reduces \( T_c \) in pure MgB\(_2\) owing to higher disorder in the lattice [91].

### 2.4.2 Critical current \((I_c)\) / critical current density \((J_c)\)

Critical current \((I_c)\) or critical current density \((J_c)\) is another important parameter in superconductors. The depairing current density \((J_d)\), which is the highest achievable current density in superconductors, is given by Equation (2.1) [92]. Around 15% of \( J_d \) can be obtained at low fields with optimized flux pinning. \( J_d \) at 0 K and magnetic field >
1 T, is around $1.3 \times 10^{12} \text{ A/m}^2$ in MgB$_2$, considering the parameters as $\lambda = 80 \text{ nm}$ and $\xi = 12 \text{ nm}$ [16].

$$J_d = \frac{\Phi_0}{3\sqrt{3} \pi \lambda^2 \xi \mu_0}$$  \hspace{1cm} (2.1)

where $\Phi_0$ is the superconducting flux quantum and $\mu_0$ is the magnetic permeability.

This value is relevant for fields above 1 T, however, at zero-field, the value increases to $2 \times 10^{12} \text{ A/m}^2$, as the $\pi$-band increases the depairing current at low fields. However, $\pi$-band charge carriers contribute only about 10% to the depairing current [6]. MgB$_2$ shows high transport current densities at low temperatures. Both the intragrain $J_c$ and intergrain $J_c$ are high for MgB$_2$. The transport $J_c$ in the wire/ tape geometry at 4.2 K is of the order of $10^6 \text{ A cm}^{-2}$ in self field and around $10^4 \text{ A cm}^{-2}$ at 8 T field [78].

The reported current densities for single crystals are small, as pinning is weak, and there is a rapid drop of $J_c$ with increasing field. They show $J_c$ of nearly $10^9 \text{ A/m}^2$ at low temperatures in self field [16, 93]. Thin films show much higher critical current densities than single crystals, owing to strong pinning at the grain boundaries. The highest $J_c$ observed so far, is $3-4 \times 10^{11} \text{ A/m}^2$ under self field at low temperatures [16].

Wires which were fabricated through the CTFF process showed values of $J_c$ of about $6 \times 10^5 \text{ A cm}^{-2}$ at 4.2 K under self field. The variation of $J_c$ with magnetic fields becomes more gradual, however, allowing larger current density values at higher field: $J_c$ at 5 T $> 10^5 \text{ A cm}^{-2}$. Tapes can achieve superior currents at relatively high magnetic fields compared to those of the wires due to their geometrical shielding properties.

Factors such as grain boundaries, porosity of the sample, presence of impurities, purity, particle size distribution of precursor materials, and sintering conditions have a strong effect on the critical currents in MgB$_2$.

The grain boundaries act as weak links and, reduce the inter-grain connectivity and $J_c$ in high temperature superconductors (HTS). The grain boundaries in MgB$_2$ are not only
transparent to current flow, but also help to improve the $J_c$ by grain boundary pinning [94]. $J_c$ can be increased by using the high-energy milling technique to reduce the grain size [30].

Porosity is one of the main factors which can reduce the transport $J_c$ in MgB$_2$ [95]. This is very hard to control in the in-situ process, however, because of the low packing density of the powder in the preparation and the evaporation of Mg during sintering. Some porosity is present in the ex-situ process, which originates from the low packing density of the powder, however, the final high temperature heat treatment plays a great role in reducing the porosity [51, 56, 61, 64, 71, 72, 96].

The purity of the precursor powder and its particle size variation are strongly affected by the final product’s grain size, grain connectivity, and superconducting properties. Some authors have found that an extra addition of Mg to the stoichiometric ingredients gives better mechanical, electrical, and superconducting properties through better grain connectivity, compared with the MgB$_2$ synthesized from stoichiometric starting elements [78, 97, 98].

Kumakura’s group has systematically studied the effects of the Mg on the critical current density [99]. They reported on improved $J_c$ due to the use of MgH$_2$ as the Mg source. MgH$_2$ releases fresh, highly reactive Mg, which favours the formation of MgB$_2$. Yamada et al. has reported on the enhancement of the transport $J_c$ values of 10 at.% SiC-doped tapes prepared from nano-size Mg powder. These values were about five times higher than those for tapes prepared with commercial Mg powder [100] The use of an ultra-fine Mg and B powder mixture prepared by ball milling resulted in a significant improvement in $J_c$ due to improved grain connectivity [101, 102].

The influence of the nature of the boron precursor on the superconducting properties has always been a main issue in the MgB$_2$ research community. Many groups have reported
systematic studies on the effects of the boron source on the critical current density, resistivity, and phase formation [103-106]. The samples made from crystalline boron powders show nearly an order of magnitude lower \( J_c \) compared to those made from amorphous precursors, which is due to the lower reactivity rate. Zhang et al. [107] reported on significant enhancement of \( J_c \) using ball-milled crystalline boron. This has been effective in increasing the reactivity of crystalline boron and achieving small grain size, which resulted in better connectivity and strong flux pinning. Recently X. Xu et al. [32] reported a systematic study on the effects of the purity of the boron powders on the superconducting properties of MgB\(_2\) using 92\% and 96\% purity boron powders as precursors. In addition to that, the same group reported a detailed study on the effects of the ball milling medium on the improvement of the superconducting properties of MgB\(_2\) [108]. Toluene has been identified as the most promising medium for ball milling among other organic solvents such as ethanol and acetone.

Grain boundaries are considered to be the most effective pinning centres in pure MgB\(_2\) [27, 50, 109, 110]. Yamamoto et al. [111] systematically analysed the relationship between the crystallinity and the irreversibility field, and their effects on the critical current density using the full width at half maximum (FWHM) values of peaks derived from powder X-ray diffraction. The FWHM of the (110) peak reflects the in-plane disorder, while the FWHM of the (002) peak reflects the out-of-plane disorder. The FWHM is apparently larger for low processing temperatures and in doped samples, owing to the reduced crystallinity. The degradation of the crystallinity originates from the disordered crystal lattice caused by various types of lattice defects or intragranular precipitates [111]. Since the pinning force at grain boundaries is inversely proportional
to the grain size and proportional to the lattice strain, both small crystal size and lattice
distortion resulted in improved grain boundary pinning.

2.4.3 Critical fields

MgB$_2$ falls onto the class of type II superconductors and is characterised by two critical
fields, called the upper critical field (H$_{c2}$) and the lower critical field (H$_{c1}$). This is an
intrinsic property defined by the $B$, $T$ phase boundary between the superconducting and
normal states of a type II superconductor. MgB$_2$ is an anisotropic material, with the
anisotropy originating from the layered structure, therefore, variation of the critical field
values can be observed from the planes parallel to and perpendicular to the $ab$-plane,
and these are denoted as $H_{c1(c2)}^\parallel_{ab}$, $H_{c1(c2)}^\perp_{ab}$. Anisotropy is very important, both for a
basic understanding of this material and for practical applications, as it strongly affects
the pinning and critical currents [5]. For textured bulk and partially oriented crystallites,
the anisotropy ratio $\gamma = H_{c2}^\parallel_{ab}/H_{c2}^\perp_{ab}$, is reported to be between 1.1 and 1.7, while for
c-axis-oriented films it is 1.2–2 and 1.7-2.7 for single crystals.
The values reported for these parameters vary depending on the purity of the sample and
hence on parameters, such as the penetration depth and the coherence length. High
purity single crystal samples have shown $H_{c1}^\parallel_{ab} = 250$ mT, $H_{c1}^\perp_{ab} = 120$ mT at 5 K
[112] and $H_{c2}^\parallel = 18$ T, $H_{c2}^\perp = 3.5$ T at 0 K [112-114]. For polycrystalline materials
the value for $H_{c1}$ at 0 K has varied from 150 to 480 Oe [19]. Pure polycrystalline MgB$_2$
shows rather low $H_{c2}$ values (16 T at 0 K), however this can be greatly improved by
chemical doping [69, 115-121]. The introduction of suitable dopants into the
superconducting matrix leads to improvement in the critical field through improved
disorder.
According to the Equation (2.2), $H_{c2}$ is determined by $\xi$. 

$$H_{c2} = \Phi_0/(2\pi\mu_0\xi^2)$$  \hspace{1cm} (2.2) 

where $\xi$ is the coherence length, $\Phi_0$ is the superconducting flux quantum, and $\mu_0$ is the magnetic permeability [111]. According to Eq.(2.2), the $H_{c2}$ of a superconducting material is inversely proportional to its coherence length, $\xi$, so $H_{c2}$ increases as $\xi$ decreases [2, 6, 111]. Therefore, the impurity scattering results in a shorter mean free path, which causes a reduction in $\xi$, thereby resulting in an increased $H_{c2}$. Introduction of disorder tends to increase the scattering in the $\sigma$- and $\pi$- bands, which then affects the critical fields [6]. The coherence length values for polycrystalline MgB$_2$ along the $ab$-plane range between 3.7 and 12.8 nm and along the $c$-axis they range between 1.6 and 5.0 nm. For single crystals they range along the $ab$-plane range between 8 and 12 nm and along the $c$-axis between 3 and 7 nm [5, 112]. As MgB$_2$ is a two-gap superconductor, the tuning of the ratio of intraband to interband scattering rates via selective doping on both Mg and B sites can improve the $H_{c2}$ and reduce the anisotropy of the critical fields.

### 2.4.4 Irreversibility field

Knowledge of the irreversibility line is important in practical applications as non-zero critical currents are confined to magnetic fields below this line. The values of irreversibility fields at 0 K range between 6 and 12 T for MgB$_2$ bulk, films, wires, tapes, and powders. The $H_{irr}$ of MgB$_2$ is $\sim$0.5$H_{c2}$, in contrast to $H_{irr}$ 0.8 $H_{c2}$ for the low temperature superconductor (LTS) material [78]. Yamamoto et al. [111] reported a strong relationship between the crystallinity and the $H_{irr}$ of MgB$_2$. According to their
results, increased disorder, which originated from the degradation of crystallinity, greatly improve the grain boundary pinning, and hence the $H_{irr}$.

### 2.4.5 Flux pinning mechanisms

As mentioned above, raising the applied field above $H_{c1}$ in a type II superconductor, leads to a mixed state in which magnetic field additionally penetrates into the superconductor in the form of thin filaments called vortices. The motion of these vortices results in resistivity, therefore, effective pinning of these vortices can widen the range of the superconductivity in type II superconductor material. Magnetic vortices can be effectively pinned at sites of atomic defects, such as inclusions, impurities, dislocations, and grain boundaries. These defects are the most effective pinning centres when their size roughly matches the size of the vortices, i.e. the coherence length.

Practical performance of superconductors is greatly affected by the effectiveness of vortex pinning, and therefore, by the type, density, and extent of the defects, as well as by $T_c$, $\xi$ and $\lambda$ [5, 6, 93, 122]. The dominant pinning centres in MgB$_2$ are considered to be grain boundaries [27, 50, 109, 123] and small MgO and Mg(B,O)$_2$ impurities in $\Delta k$-pinned grains also contribute to better pinning [24, 40].

According to the model proposed by Dew-Hughes for pinning mechanisms, the normalized pinning force density can be expressed as in Equation (2.3) [122].

$$ F_p(b) = \frac{F_p}{F_p^{\max}} \propto b^p(1-b)^q $$  \hspace{0.5cm} (2.3)

Where the dimensionless parameters $p$ and $q$ depend on the specific characteristics of flux pinning in the superconductor, and $b$ is the reduced field ($H/ H_{c2}$ or $H/ H_{irr}$).

Under this model, six different pinning mechanisms are defined, depending on the $p$ and $q$ values [5].
I. \( p = 0, q = 2 \) : normal core pinning, volume pins

II. \( p = 1, q = 1 \) : \( \Delta k \)-pinning, volume pins

III. \( p = 1/2, q = 2 \) : normal core pinning, surface pins

IV. \( p = 3/2, q = 1 \) : \( \Delta k \)-pinning, surface pins

V. \( p = 1, q = 2 \) : normal core pinning, point pins

VI. \( p = 2, q = 1 \) : \( \Delta k \)-pinning, point pins

Although this model can be used to analyse the pinning mechanisms present in MgB\(_2\), it was not been used frequently in this study, as the p and q parameters obtained from the fitted results do not fall onto any of the above values.

Instead, another frequently used pinning mechanism based on the vortices and pinning centres which has been proposed by Qin et al. [124] has been used in this study. The two mechanisms involved in the core interaction are \( \delta T_c \) pinning and \( \delta l \) pinning. The \( \delta T_c \) pinning is caused by the spatial variation of the Ginzburg-Landau (GL) coefficient \( \alpha \) associated with disorder in the \( T_c \), and the \( \delta l \) pinning is caused by the variation of the charge-carrier mean free path \( l \) near lattice defects. This model is used to analyse the solid vortex region in terms of the single vortex, small-bundle, and thermal fluctuation regimes, depending on the applied magnetic field. The crossover field, \( B_{sb} \), is defined as the field separating the single vortex regime from the regime where the vortices form small bundles, below which the \( J_c \) is almost independent of the applied field.

The variation of \( B_{sb} \) with reduced temperature \( t = T/T_c \) for \( \delta T_c \) and \( \delta l \) pinning is given by Equation (2.4) and (2.5), respectively:

\[
B_{sb} = B_{sb}(0) \left[ \frac{1-t^2}{1+t^2} \right]^{2/3} \tag{2.4}
\]

\[
B_{sb} = B_{sb}(0) \left[ \frac{1-t^2}{1+t^2} \right]^{2} \tag{2.5}
\]
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This has been discussed in detail, with reference to the experimental data in Chapter 4 and Chapter 7.

2.4.6 Resistivity

According to the resistivity analysis by Rowel et al. [125] a wide range of resistivity has been reported for MgB₂ so far. The resistivity at room temperature varies from 20 μΩ cm up to 100 mΩ cm, covering all the sample types from bulk to thin films. The high resistivities seen in many samples are due to poor connectivity, that is, due to the reduction of effective cross-sectional area of the sample. This results in a reduction in \( J_c \), however, the active cross-sectional area alone does not explain the resistivity behaviour of MgB₂. The presence of insulating precipitates in or in between grains, the presence of porosity and the substitution of atoms, such as, carbon for boron, are some of the factors that can affect the resistivity of MgB₂.

The normal state resistivity in metals is based on two contributions, the temperature dependent residual resistivity, \( \rho_0 \), originating from electron scattering at defects and a phonon-mediated contribution, \( \rho_{ph} \), which increases with temperature [16].

\[
\rho(T) = \rho_0 + \rho_{ph}(T) \quad (2.6)
\]

For the two-band conductors, however, the resulting resistivity is given by the Equation (2.7), considering the two band conductivity.

\[
1/\rho(T) = 1/\rho(\sigma(T)) + 1/\rho(\pi(T)) \quad (2.7)
\]

The resistivity is greatly affected by scattering at both the \( \sigma \)- and \( \pi \)-bands at low temperatures; however, the \( \pi \)- band dominates at room temperature. The presence of defects reduces the mean free path of the charge carriers in both bands. The temperature
dependence of the resistivity in MgB\textsubscript{2} obeys a power law according to Equation (2.8), which is expected for metals according to the Bloch–Gruneisen behaviour.

\[ \rho(T) = \rho_0 + aT^n, \]  
\[ \text{(2.8)} \]

where, \( \rho_0 \) is the residual resistivity, \( a \) is a parameter, and \( n \) is the power law dependence of the resistivity, which indicates the disorder of the material [126]. This model has been used to analyse resistivity in this study.

In addition, the resistivity near the transition has been used to analyse the dependence of the flux-flow activation energy, \( U_0 \), using the model proposed by Sidorenko et al. [127], which is used to understand the mechanism of flux creep or flux flow in MgB\textsubscript{2}, based on the thermal activation of flux line motion over the energy barrier \( U_0 \) of the pinning centres.

In this model, the thermally activated flux flow is expressed by the Equation (2.9).

\[ \rho(T, B) = \rho_0 \exp\left[-\frac{U_0}{k_B T}\right] \]  
\[ \text{(2.9)} \]

Here, \( U_0 \) is the flux-flow activation energy, which can be obtained from the slope of the linear part of the Arrhenius plot, \( \rho_0 \) is a field independent pre-exponential factor, and \( k_B \) is Boltzmann’s constant. This has been discussed in detail, with reference to the experimental data in Chapter 4 and Chapter 7.

2.5 Effects of doping on the superconductivity of MgB\textsubscript{2}

The critical current density can be improved by several techniques, such as, chemical doping, ball milling, thermo-mechanical processing and proton irradiation. Chemical doping, however, is considered as an especially easy and effective way of enhancing the superconducting properties of MgB\textsubscript{2}.
The effects of doping can be classified into two categories as substitution and addition effects. In the substitution effect, the dopant will substitute into the B or the Mg crystal sites, which will then result in impurity scattering of charge carriers and yield changes in the electronic state, lattice distortions, and crystallinity. The addition effects, in contrast, will only act between the grains, producing a substantial effect on the grain growth and grain connectivity [119].

Although chemical doping offers various benefits in terms of improving the superconducting properties of MgB$_2$, $T_c$ is affected adversely. Eisterer et al. [16] has pointed out four mechanisms that can potentially reduce the $T_c$, reduction of the density of states (DOS), reduction of the $\sigma$-gap anisotropy, hardening of the $E_{2g}$ phonons, and intraband scattering. Changes in the lattice parameter affects the $T_c$, as this changes the DOS and also affect on the $E_{2g}$ phonon frequency [16, 86, 87, 90, 128, 129]. The highest $T_c$ reported was 41.8 K for thin MgB$_2$ layers on boron crystals or for films grown on SiC [16].

So far, many dopants such as metal elements (Ti, Zr, Mo, Fe, Co, Ni, Cu, Ag, Al, Si, La etc..), metal oxides (Al$_2$O$_3$, HoO$_2$, MgO, TiO$_2$, SiO$_2$, PrO$_{11}$, etc.), carbon and carbon inorganics (nano-C, C nanotubes, nano diamond, TiC, SiC, B$_4$C, Na$_2$CO$_3$, etc.), nitrides, borides and silicides (Si$_3$N$_4$, ZrB$_2$, TiB$_2$, NbB$_2$, CaB$_6$, WSi$_2$, ZrSi$_2$, etc.) and organic compounds (malic acid, maleic anhydride, paraffin, carbohydrate, toluene, ethanol, acetone, and tartaric acid) have been doped into MgB$_2$. The effects of doping those elements on the superconductivity of MgB$_2$ have been reported by many groups around the world [6]. Due to the large number of possible dopants, as can be seen from above paragraph, it is not possible to summarize the effects of each dopant on the superconductivity of MgB$_2$. Only the effects of some dopants, which showed
considerable positive or highly negative impact on the superconductivity of MgB$_2$, will briefly be discussed here.

### 2.5.1 Effect of carbon (C) doping on the superconductivity of MgB$_2$

The metallic elements and metal oxides were included for the purpose of introducing normal flux pinning centres, however, borides, nitrides, and C-containing dopants were added both to increase $H_{c2}$ and to introduce pinning centres [6].

The following improvements can be observed through proper doping.

- Increased $H_{c2}$ and the $H_{irr}$ through impurity scattering.
- A wide distribution of point pinning centres can be formed.
- Localized lattice strains can be produced, which also favours on flux pinning.

Among the other dopants, C doping shows the most significant improvement in the superconducting properties of MgB$_2$, and abundant research work has been carried out so far to study this phenomenon. C doping is aimed at substitution of carbon into boron sites in MgB$_2$, and it has a great impact on the carrier density, as carbon has one more electron than boron, and would donate electrons to the $\sigma$-band, hence modifying the superconducting properties such as $J_c$, $H_{c2}$, and $H_{irr}$ [5, 6, 119]. Carbon doping, however, adversely affects the transition temperature, which is mainly due to the disorder originating from impurity/defect formation within the MgB$_2$ grains [90, 91, 118, 119].

According to band structure calculations of MgB$_2$ electron doping causes a reduction in the density of states (DOS) at the Fermi Level ($E_F$) [130]. The theoretical calculations
show that the DOS at $E_F$ decreases due to the effects of carbon doping on boron sites [131]. The phonon spectra shows a considerable peak shift of the $E_{2g}$ mode towards higher energies in carbon doped MgB$_2$ compared to the undoped MgB$_2$ [132, 133].

Owing to the difference between the nominal and actual C substitution levels, the reported solubility of C in MgB$_2$ and its influence on the superconductivity vary considerably, depending on the inhomogeneities that originate from the precursor materials, and the fabrication techniques and processing conditions used. In early studies on the carbon solubility, figures ranging from 1.25% to 30% were reported when elemental magnesium, boron, and carbon were used as precursors, however, the actual carbon level is different from the nominal composition [134]. Carbon doping results in an anisotropic lattice concentration and a substantial reduction in T$_c$. The $a$- lattice parameter is greatly affected by the C doping while the $c$- parameter is only slightly affected or unaffected.

A neutron diffraction study carried out to estimate C concentration by Avdeev et al. [129] revealed a linear relationship between the unit cell parameter $a$ and the C concentration. According to that relationship, the level of C substitution, $x$ in the formula of Mg(B$_{1-x}$C$_x$)$_2$, can be estimated as,

$$x = 7.5 \Delta (c/a) \quad (2.10)$$

where $\Delta (c/a)$ is the change in c/a compared to the pure sample [129].

S. Jemima et al.,[135] have evaluated the actual C fraction substituted into the polycrystalline MgB$_2$ matrix by the conventional solid–vapour reaction route and discovered that the actual composition is in disagreement with the nominal composition. Since carbon doping resulted in a significant enhancement of the superconducting properties of MgB$_2$, a large number of carbon sources have been studied as dopants.
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The common dopants used in MgB$_2$ are SiC [136-138], nano-carbon [54, 69], carbon nano tubes (CNTs) [117, 139], graphite [118], boron carbide (B$_4$C)[140-142], nano-diamond, hydrocarbons [121, 143-146], carbohydrates [147, 148], and graphene [149-151] (which was rather recently revealed as an effective dopant).

The improvement achieved through SiC is remarkable, and many groups have reported on the effects of the precursor size, the sintering conditions, the optimum doping levels, and the different fabrication techniques for SiC-doped MgB$_2$ [63, 137, 152-156]. A significant breakthrough in enhancing $J_c$ was achieved using nano-SiC doping into MgB$_2$ matrix. At the doping level of 10 wt% SiC, MgB$_2$ bulk samples showed $H_{irr}$ of 8 T and $J_c$ of $10^5$ A cm$^{-2}$ under 3 T at 20 K, with a slight reduction in $T_c$ [157]. It was also shown that carbon substitution for boron resulted in a large number of intra-granular dislocations and dispersed nano-size impurities, which are jointly responsible for the significant enhancement in flux pinning. Another effect of addition or substitution of carbon or SiC is that it will create more microscopic defects acting as electron scattering centres, which then serves as pinning centres [48]. Recently, Matsumoto et al. [158] reported very high values of $H_{c2}(0)$ exceeding 40 T for SiC-doped bulk MgB$_2$ sintered at 600 ºC.

Due to the improved reactivity, nano-carbon doped MgB$_2$ can synthesizes at lower temperatures, with a considerable substitution of C in boron sites. A better enhancement of the superconducting properties was observed in nano-C doped MgB$_2$ tapes, which sintered at 750 ºC. It showed transport $J_c$ for the 5 at% C-doped tape that reached $1.85 \times 10^4$ Acm$^{-2}$ at 10 T and $2.8 \times 10^3$Acm$^{-2}$ at 14 T, respectively, both at 4.2 K [54].

Among the various carbon precursors, the use of CNT is significant due to its capability of improving the mechanical and thermal properties of MgB$_2$ wires. The best performances in $J_c$ was observed in the single wall carbon nano tubes (SWCNT) doped
samples sintered at 900°C [119]. The uses of CNT, however, are limited due to the presence of the entanglements and the agglomerates, which block the transport current. The use of ultrasonication to mix CNT with MgB$_2$, however, provides a homogeneous mixing, which resulted in a significant improvement in $J_c$ [139].

It was reported that enhanced $H_{c2}(T = 0)$, for pure MgB$_2$ from 16.0 to 32.5 T in a carbon doped MgB$_2$ filament, with slight depression of $T_c$ from 39.2 to 36.2 K for 3.8% of C substitution, could be achieved by using the chemical vapour deposition (CVD) method [159]. B$_4$C is another successful C source for MgB$_2$, which improves the superconducting properties under high magnetic fields due to the relatively low processing temperature and carbon substitution effects. A $J_c$ value of $10^4$ A cm$^{-2}$ at 4.2 K and 9 T for MgB$_2$/Fe wires with 10 wt% B$_4$C powders was reported recently [140].

Apart from the carbon sources mentioned so far, the uses of hydrocarbons and carbohydrates as dopants has specific advantages over the other carbon dopants, resulting in $J_c$ values almost comparable with those from the best SiC nanopowder doping [143, 144, 160, 161]. Since most of the organic reagents decompose at temperatures below the formation temperature of MgB$_2$, highly reactive and fresh C on the atomic scale can be introduced, and hence, the carbon substitution for boron can take place at as low temperature as the formation temperature of MgB$_2$. This would leads to a better $J_c$ enhancement due to the benefit from homogenous mixing in the liquid state, and a smaller MgB$_2$ grain size due to the low sintering temperature.
2.5.2 Effects of graphene doping on the superconductivity of MgB$_2$

Although 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, most of these dopants adversely affects the performance of $J_c$ at low field, mostly due to the high doping level and poor intergrain connectivity due to precipitates. A high level of doping causes substantial reduction of $T_c$ as well.

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 at very low doping levels. The effect of doping on $T_c$ is also insignificant due to the improved crystallinity acquired through long sintering conditions and induced tensile strain in the matrix due to doping [149, 151, 162, 163] (See Figure 2.6).

Lattice parameter variation with respect to the doping level of the graphene doped MgB$_2$ is also not very pronounced, as with other carbon sources. The thermal stability of graphene is very high due to its unique structure, and therefore, graphene is a stable carbon source during the solid–liquid reaction of MgB$_2$ formation. Only partial substitution was observed on boron sites, while a considerable amount remained un-reacted [163]. In addition, the presence of strong tensile strain counteracts the lattice shrinkage due to carbon substitution. Transmission electron microscope images, which show a relatively high density of defects with fringes, are further evidence of the presence of tensile strain in the MgB$_2$ matrix [151, 163]. These defects are capable in improving the flux pinning and result in a significant improvement in the $J_c$ performance. Scanning electron microscope images of graphene doped MgB$_2$, show a nicely formed well-connected grain structure, and this together with the resistivity
analysis gives the evidences of improved grain-to-grain connectivity. Based on above facts, we suggest that graphene doping can improve the superconducting properties of MgB$_2$, both at low and high magnetic fields.

![Graphene doping in MgB$_2$ superconductors](image)

Figure 2.6: Comparison of T$_c$ dependence on carbon content in MgB$_2$ for graphene and nano-carbon doping [168]. The inset shows the second derivative of the T$_c$ dependence on graphene content to indicate the concave up behavior.

Graphene is single layered carbon with a honeycomb arrangement of atoms [164-166], which is very similar to the structure of the boron layer in MgB$_2$. Unlike the other carbon sources, graphene possesses very low electrical resistivity [164], which can be of benefit to the current carrying ability of MgB$_2$ superconductors.
A graphene single sheet is a two-dimensional sheet of sp$^2$-hybridized carbon and is expected to have tensile modulus and ultimate strength values similar to those of single wall carbon nanotubes (SWCNTs). Long-range $\pi$-conjugation in graphene yields extraordinary thermal, mechanical, and electrical properties [164, 165, 167]. Experimental results from transport measurements showed that graphene has a remarkably high electron mobility at room temperature, with reported values in excess of 15,000 cm$^2$V$^{-1}$s$^{-1}$[168]. The resistivity of a graphene sheet would be $10^{-6}$ $\Omega$ cm, less than the resistivity of silver, the lowest resistivity substance known at room temperature. The near-room temperature thermal conductivity of graphene is between $(4.84\pm0.44) \times 10^3$ and $(5.30\pm0.48) \times 10^3$ Wm$^{-1}$K$^{-1}$[169].

Generally, the acronym GO refers to the exfoliated graphite oxide, existing in the form of single sheets or a few stacked sheets. There have been different procedures reported for the reduction of graphene oxide (GO), including chemical reduction, thermal annealing, microwave irradiation, etc [170-174]. Hydrazine and its derivatives are reported as effective reducing agents for the preparation of chemically converted graphene (CCG). It was recently reported that some sulphur-containing compounds, such as NaHSO$_3$, Na$_2$S.9H$_2$O, SOCl$_2$, Na$_2$S$_2$O$_3$, and SO$_2$, can be used as reducing agents to reduce GO in aqueous solutions [173]. These synthesis methods, however, are complex in nature and still unrealistic for large-scale production. Instead GO can be used as a precursor, with a following thermal reduction, by which it is then reduced to graphene [174, 175]. In fact, this is more beneficial for large-scale production due to its simplicity. In addition, GO is a relatively cheap material and possesses the advantage of easy dispersion in organic solutions, which is still unrealistic with graphene. This provides a homogeneous dispersion of the dopant in the matrix, which can improves its effectiveness substantially. Our group was
the first to investigate the effects of GO doping on the superconducting properties of MgB\(_2\) (which is reported in the Chapter 7), therefore, still there is no other literature available under this topic.

### 2.5.3 Effect of other doping materials on the superconductivity of MgB\(_2\)

Many reports have shown that Al substitution at the Mg sites results in a serious degradation of \(T_c\) due to the change in the carrier density and density of states at the Fermi surface \([176, 177]\). Berenov et al. \([178]\), however, reported on enhancement of \(J_c\) in self field at 20 K, together with an increase in the upper critical field due to doping. The critical temperature of that sample was also only slightly affected by the low doping level.

Several groups have reported on the effects of Ti doping into MgB\(_2\) in bulk, wire, and tape forms, and all the reports showed positive effects on the superconductivity of MgB\(_2\) \([179-182]\). Zhao et al have observed a nano-layer of TiB\(_2\) at the grain boundaries of MgB\(_2\), forming a strongly coupled nanoparticle structure. They claim that this contributes significantly to improved flux pinning, thereby improving \(J_c\) performance \([181]\).

A new processing method for doping Ti into MgB\(_2\) has been reported using the chemical vapour deposition (CVD) method \([183, 184]\). It was found that CVD methods are an effective way to distribute the Ti impurities and can be used to produce conductors with very high \(J_c\) values. The samples showed a fine dispersion of Ti throughout the grains, and they did not observe any with precipitation of TiB\(_2\) on MgB\(_2\).
grain boundaries, as was observed for samples prepared by the solid state reaction method.

Dou et al. [185] reported on the effects of nano scale Fe doping on MgB₂, which was shown to adversely affect on the $J_c$ performance. They proposed that the degradation of $J_c$ was due to both the Fe substitution for boron in the lattice structure and the inclusions of Fe and FeB which act as weak links at grain boundaries.

In addition to above dopants, an increase in the $J_c$ performance at low field was observed from doping with small amounts of Si [176], Zr [179, 180], Ta [38], and Ag [186]. MgO phase is always present with the main phase of MgB₂ as the major impurity phase, and the effects of the presence of MgO have been reported by several groups, as discussed in detail in section 2.3.1. iang et al. [187] reported that doping with nano-MgO (2.5 wt.%) is capable of increasing the $J_c$ performance of MgB₂ tapes due to the improvement in the grain connectivity and core density. Later, Perner et al. [188] discovered that doping with microsizes MgO can also improve $J_c$, mainly due to the improved flux pinning.

Shen et al. [189] found that $J_c$ of bulk polycrystalline MgB₂ is significantly enhanced by doping with Bi-2212. Microstructural analysis indicates that the undecomposed Bi-2212 particles remain in the MgB₂ matrix, where they act as effective pinning centres.

Haruta et al. [190] reported that the effective pinning centres can be introduced by deposition of a MgB₂ thin film in an O₂ atmosphere. The $J_c$ of the oxygen doped film was higher than that of the non-doped film in magnetic fields applied both perpendicular and also parallel to the $c$-axis.
2.3.4 Summary of parameters of MgB$_2$

Most of the properties discussed throughout the literature review, are summarized in Table 2.1 for ease of referring in the thesis [2].

Table 2.1: List of superconducting parameters of MgB$_2$ [80]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Critical temperature</td>
<td>39 ~ 40 K</td>
</tr>
<tr>
<td>Lattice parameters</td>
<td>$a = 0.3086$ nm</td>
</tr>
<tr>
<td></td>
<td>$c = 0.3524$ nm</td>
</tr>
<tr>
<td>Theoretical density</td>
<td>$\rho = 2.55$ gcm$^{-3}$</td>
</tr>
<tr>
<td>Resistivity near $T_c$</td>
<td>$\rho (40$ K$) = 0.4$ ~ $16$ $\mu$Ω cm</td>
</tr>
<tr>
<td>Resistivity ratio</td>
<td>$RR = \rho (300$ K$)/\rho (40$ K$) = 1$ ~ $27$</td>
</tr>
<tr>
<td>Upper critical field</td>
<td>$H_{c2//ab(0)} = 14$ ~ $39$ T</td>
</tr>
<tr>
<td></td>
<td>$H_{c2//c(0)} = 2$ ~ $24$ T</td>
</tr>
<tr>
<td>Lower critical field</td>
<td>$H_{c1(0)} = 27$ ~ $48$ mT</td>
</tr>
<tr>
<td>Irreversibility field</td>
<td>$H_{irr} = 6$ ~ $35$ T</td>
</tr>
<tr>
<td>Coherence length</td>
<td>$\xi_{ab(0)} = 3.7$ ~ $12$ nm</td>
</tr>
<tr>
<td></td>
<td>$\xi_{c(0)} = 1.6$ ~ $3.6$ nm</td>
</tr>
<tr>
<td>Penetration depth</td>
<td>$\lambda(0) = 85$ ~ $180$ nm</td>
</tr>
<tr>
<td>Energy gap</td>
<td>$\Delta(0) = 1.8$ ~ $7.5$ meV</td>
</tr>
</tbody>
</table>
2.4 References


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CHAPTER 2: Literature review on Magnesium Diboride (MgB₂)


CHAPTER 2: Literature review on Magnesium Diboride (MgB₂)


Chapter 3: Experimental Details

3.1 Sample preparation

3.1.1 Fabrication of MgB₂ bulk samples

MgB₂ bulk samples were prepared by the diffusion method from crystalline boron powder (0.2 to 2.4 μm, 99.999%), Mg powder (99%, 352 mesh), and the dopant (i.e. graphene, reduced graphene, or graphene oxide) as precursors. Initially, boron was separately mixed with a suitable amount of dopant in a mortar. Powders were then pressed, using a uni-axial press under a pressure of 8000 psi, into pellets 13 mm in diameter, and then inserted into a soft iron tube with the stoichiometric ratio of Mg to B, plus 20% excess Mg to compensate for the loss of Mg during sintering. The samples were sintered at 800°C for 10 h in a quartz tube furnace at the heating rate of 5°Cmin⁻¹ under high purity argon (Ar 99.9%) gas.

3.2 Equipment

3.2.1 Phase and Structure Characterization

3.2.1.1 X-ray Diffraction

X-ray diffraction (XRD) was used to examine the phase formation and obtained patterns were evaluated to investigate the phases, lattice parameters, micro-strains and grain sizes. In this work, XRD was performed in the step-scanning mode θ - 2θ by using a Philips GBCMMA diffractometer with a Cu-Kα radiation source (λ = 1.54059 Å).
Typically, diffraction data was collected from 10º – 105º in a step width of 1º and counting time per minute. The XRD patterns were obtained on powdered samples that were attached to a glass slide using small amount of ethanol.

X-ray diffraction is based on constructive interference of monochromatic X-rays from a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate them, and directed toward the sample. Peaks in the XRD pattern were indexed using Bragg’s law of \( 2d \sin \theta = n \lambda \), where, \( n \) is an integer, \( \lambda \) is the radiation wave length, \( \theta \) is the diffraction angle and \( d \) is the inter-planer distance.

XRD patterns were used to calculate the lattice parameters using the Rietveld refinement method. The strain and the grain size details were calculated from Williamson-Hall plots.

### 3.2.1.2 Scanning electron microscopy (SEM)

In this work, the scanning electron microscope (SEM) was used to investigate the microstructure, morphology, and chemical compositions of the samples. 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. The SEM uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The electrons emitted from the sample are then collected and used to form the image of the sample. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in scanning mode using conventional SEM techniques. The SEM unit is also capable of performing analyses of selected point locations on the sample, which is especially useful in
qualitatively or semi-quantitatively determining chemical compositions (using energy dispersive X-ray (EDX) analysis).

### 3.2.1.3 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) in this study was performed on powdered and focussed ion beam (FIB) samples using a JEOL 2011 200 keV analytical instrument. Compared to SEM, TEM provides higher resolution (0.2 nm), which is capable of revealing more details of the microstructure.

In the TEM technique, the image is formed based on the interaction of a beam of transmitted electron with an ultra-thin specimen. The most common mode of operation of TEM is the bright field imaging mode. Here, in this mode, the contrast of the image is formed due to the absorption of electrons in the sample. The microstructure, e.g., the grain size, can be studied by the use of the image mode, while the crystalline structure is studied by the diffraction mode. The diffraction patterns reveal the details of crystal defects, such as dislocations, stacking faults etc. Apart from that, the chemical composition of small volumes, e.g., grain boundaries, can also be obtained by detection of X-rays emitted by the film. A simple schematic representation of the image forming technique in TEM is shown in the Figure 3.1 [1].

![Figure 3.1: Schematic representation of the image forming technique in TEM](image-url)
3.2.1.4 Raman scattering measurements

In this work, the Raman scattering was measured using a confocal laser Raman spectrometer (HORIBA Jobin Yvon system) with a 100× microscope. The 632.8 nm line of a HeNe laser with power of about 20 mW was used for excitation.

Raman spectroscopy allows the detection and identification of molecules through their unique vibrational and rotational energy level structure. Raman scattering relies on inelastic scattering of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. When this laser light interacts with the molecules and phonons in the system (in the sample), it results in a shift in the energy of the photons. This shift in energy reveals information about the vibrational modes in the sample. The intensity of the weak inelastically scattered light is measured as a function of the frequency shift. Figure 3.2 shows a schematic representation of Raman spectroscopy.

![Schematic representation of Raman spectroscopy](image)

Figure 3.2: Schematic representation of Raman spectroscopy [1].
3.2.1.5 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) analysis was carried out using Al K\(\alpha\) radiation (with the photon energy of 1486.6 eV) and a PHOIBOS 100 hemispherical energy analyser from SPECS. The data were processed using commercial CasaXPS software.

XPS is a quantitative spectroscopic technique that analyses the surface chemistry of a material. In particular, it can measure the elemental composition, empirical formula, chemical state, and electronic state of the elements that exist within a material. XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and number of electrons, which escape from the top 1 to 10 nm of the material being analysed.

3.2.2 Electromagnetic property characterization

Electromagnetic properties such as the critical temperature \((T_c)\), the critical current density \((J_c)\), and the critical fields \((H_{c2}\) and \(H_{ir}\)) of the superconducting material were measured using a Quantum Design physical property measurement system (PPMS).

In magnetic measurement, the sample is placed in a system of primary and secondary coils. The primary coil produce an excitation field set to amplitude of 0.1 Oe and frequency of 117Hz. The sample is placed in the secondary coils, where the change in the induction voltage through the coil due to the shielding current can be detected by the lock-in amplifier (see Figure 3.3).

In the transport measurements, the sample needs to be prepared in a particular way, so the sample is put into a holder where it is contacted through the four probe method. The two outer contacts in the probe are to measure the current through the sample, while the
two inner contacts in the probe are to measure the voltage. In addition, the same method can be used to measure the room temperature resistivity of the sample, with sensitivity up to 1 $\mu\Omega$.

3.2.2.1 Determination of the critical temperature, $T_c$

$T_c$ of the superconducting materials was determined by magnetic susceptibility measurements or by transport measurements. Both of these measurements were performed using a Quantum Design physical property measurement systems (PPMS).

In the magnetic measurement, $T_c$ is defined as the onset of the diamagnetism by measuring the real part of the ac susceptibility with a sensitivity of up to $10^{-8}$emu. In the transport measurement method, $T_c$ is defined as the onset of the resistivity drop to zero point. Figure 3.4 shows the $T_c$ definition based on the transport measurement method.

The residual resistivity, $\rho_0$, an indicator of the impurity scattering effects, is defined as the resistivity at the transition point. By further analysis of the resistivity dependence of
temperature plot, the following important parameters were calculated and are discussed throughout the thesis.

The active cross-section ($A_F$) was calculated from the resistivity, $\rho$, from Rowell’s model, [2], using the following Equations:

$$\Delta \rho_{\text{ideal}} = \rho_{\text{ideal (300K)}} - \rho_{\text{ideal (40K)}}$$

(3.1)

where $\rho_{\text{ideal}}$ is the resistivity of a fully connected sample made from high purity sources, for which $\Delta \rho_{\text{ideal}} = 4.3 \ \mu\Omega \ \text{cm}$. The active area fraction is given by the equation

$$A_F = \frac{\Delta \rho_{\text{ideal}}}{[\rho_{\text{(300K)}} - \rho_{\text{(40K)}}]}$$

(3.2)

3.2.2.2 Determination of the critical current density, $J_c$

The critical current density, $J_c$, can be measured through the variation of the moment under different magnetic fields from the DC magnetization measurement. This was carried out on MgB$_2$ samples using the Quantum Design physical property measurement system (PPMS). The sample moves in a constant magnetic field and the waveform signal from the sample is picked up by detection coil. The signal is then fitted
with the known calibration waveform, where the magnetic moment of the sample is a fitting parameter. The magnetic hysteresis loop was measured over a temperature range of 5 to 30 K in a time-varying magnetic field with sweep rate 50 Oe/s and amplitude 8.5T.

The magnetic $J_c$ was derived from the width of the magnetization loop using Bean’s model [3].

![Magnetic hysteresis loop](image)

Figure 3.5: Schematic presentation of magnetic hysteresis loop of a superconductor, showing the width of the loop $\Delta M$.

The Equation used for a bar shaped sample is,

$$J_c = 20 \frac{\Delta M}{a(1-a/3b)V}$$

(3.3)

Here, $\Delta M$ is the width of the relevant M (H) loop, $a$ and $b$ are the width and length of the bar shaped sample, respectively, in a plane perpendicular to the applied field, (with $a < b$) and $V$ is the volume of the sample.

The dimensions for each sample were kept at nearly 1 mm, 2 mm and 3 mm in all cases, to reduce the effect of the size factor on the $J_c$ results. Figure 3.5 shows the schematic presentation of magnetic hysteresis loop of a superconductor, defining the $\Delta M$. 
3.2.2.3 Determination of the upper critical field, $H_c$ and irreversibility field $H_{irr}$

The upper critical field ($H_{c2}$) and the irreversibility field ($H_{irr}$) were determined using the resistivity versus temperature plot which was measured in the Quantum Design PPMS up to 13 T. The $H_{c2}$ and $H_{irr}$ were obtained by measuring the temperature at which the normal state resistivity of the sample dropped by 90% and 10% respectively. This has been used as a standard by many research groups to present their data; therefore this is the criterion which has been used to calculate the critical fields in this thesis to have a consistent representation of the results of this study as well as for ease in comparing other results peoples’ results with the results of this study. Figure 3.6 shows the resistivity dependence on the temperature under different applied magnetic field and the dotted lines represent the definitions of $H_{c2}$ and $H_{irr}$.

From the magnetization measurements, $H_{irr}$ was assumed based on a criterion, the field at which the $J_c = 100$ A cm$^{-2}$ at a particular measuring temperature.
Figure 3.7: $H_{0r}$ determined by using the criterion of $J_c = 100 \text{ A cm}^{-2}$

### 3.3 References


Chapter 4: Effects of Graphene Doping on the Superconductivity of MgB\textsubscript{2}

4.1 Introduction

The discovery of superconductivity in MgB\textsubscript{2} at 39 K has attracted great interest around the world, due to its high critical temperature ($T_c$), which is the highest among the intermetallic superconductors [1]. Improvements in critical current density ($J_c$) in the presence of applied magnetic field, the upper critical field ($H_{c2}$), and the irreversibility field ($H_{irr}$), have been key issues in MgB\textsubscript{2} superconductors, as the critical current density of pristine MgB\textsubscript{2} drops rapidly with increasing magnetic field, which is mainly due to its poor flux pinning and low $H_{c2}$. Many groups have shown that a significant enhancement of $J_c$ in high magnetic fields can be obtained by doping with nanoparticles such as from various carbon sources, SiC, and silicon oil [2-9]. Carbon can be considered as the most successful dopant for enhancing $H_{c2}$, as it causes strong intraband electron scattering in the σ and π bands of B-B bonds. On the other hand, the introduction of nanoparticles can result in improved flux pinning because they form point pinning centres, as well as producing lattice strains which can lead to lattice defects. The carbon doping, however, comes with its own drawback of reducing $T_c$, which limits the application temperature of MgB\textsubscript{2} [10].

Graphene is becoming recognized as a novel dopant for MgB\textsubscript{2}, with its unique properties stemming from its semi-metallic nature. Our group was the first to find that chemical doping of MgB\textsubscript{2} with graphene can notably improve $J_c$ with only a slight reduction in $T_c$ [8]. The method for the synthesis of graphene used in this study has been optimised to produce bulk quantities and so that it can be exploited for commercial
production. Therefore, our chemical doping of MgB$_2$ with graphene is focused on using the technology for commercial application. Graphene is single layered carbon with a honeycomb arrangement of atoms [11-13], which is very similar to the structure of the boron layer in MgB$_2$. Unlike the other carbon sources, graphene possesses very low electrical resistivity[11], which can be of benefit to the current carrying ability of MgB$_2$ superconductors. On the other hand, the difference between the thermal expansion coefficients of graphene and MgB$_2$ could lead to the development of microstrains in the matrix, resulting in lattice defects which are capable of improving flux pinning [8, 14-17]. The focus of this study is on improving our understanding of the microstructural changes that occur due to doping and their effects towards enhancing the superconducting properties of MgB$_2$.

4.2. Experimental details

4.2.1 Sample preparation

Graphene doped bulk samples were prepared via the diffusion method from crystalline boron powder (0.2 to 2.4 µm 99.999%), Mg ingot (99.84%), and highly reduced chemically converted graphene (rCCG) as precursors. Highly reduced chemically converted graphene (rCCG) was obtained by excess reduction of an aqueous dispersion of chemically converted graphene (CCG), as reported by Dan Li et al., [18], using hydrazine at the refluxing temperature. The resulting rCCG agglomerates were dried completely and further treated with an excess quantity of thionyl chloride, as reported by Eda et al., [19] to further improve the electrical conductivity.
Initially, boron and graphene powders were mixed by hand milling according to the formula \( \text{MgB}_{2-x},C_x \), where \( x = 0, 1, 3 \) and 5 mol % graphene. Powders were then pressed into pellets 13 mm in diameter and inserted into a soft iron tube with the stoichiometric ratio of Mg to B, plus 20% excess Mg to compensate for the loss of Mg during sintering. The samples were sintered at 800°C for 10 hours in a quartz tube at a heating rate of 5°C min\(^{-1}\) under high purity argon (Ar 99.9%) gas.

### 4.2.3 Equipment used

The phase identification and crystal structure investigations were carried out using an X-ray diffractometer (GBCMMA) with Cu-K\( \alpha \) radiation (\( \lambda = 1.54059 \) Å). The Raman scattering was measured using a confocal laser Raman spectrometer (HORIBA Jobin Yvon system) with a 100× microscope. The 632.8 nm line of a HeNe laser with power of about 20 mW was used for excitation. A detailed description of the equipments used is available in Chapter 3.

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 [20] from a physical properties measurement system (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 \( (A_F) \) was calculated from the resistivity, \( \rho \), from Rowell’s model, [21].
4.3. Results and discussion

4.3.1 Characterization

The doping level of 5 at.% was selected for the over-doped sample, to give a better contrast and achieve a better understanding of the effects of doping. Figure 4.4, however, gives the details on the 3 at. % doping level also, to show the effects of increasing the doping level systematically. Figure 1 presents the room temperature X-ray diffraction patterns (XRD) of undoped and graphene (G) doped MgB$_2$ bulk samples. The XRD measurements were performed on the ground MgB$_2$ pellets. They show all the Bragg reflections of the hexagonal MgB$_2$ structure, plus some additional peaks which represent Mg phase. Moreover, the peak near 62º which represents MgO (220) cannot be observed in these samples, revealing that the formation of MgO during sintering is reduced in the diffusion method compared to the in-situ method.

Figure 4.1: XRD patterns of undoped and G-doped MgB$_2$ bulk samples.
Table 4.1 shows the lattice parameters $a$ and $c$, the $c/a$ ratio, and the full width at half maximum (FWHM) of the (110) diffraction peak values of undoped and G-doped MgB$_2$ bulk samples. The refinement results reveal that the $a$-parameter is slightly reduced with increasing doping level, which indicates that carbon is substituted into B sites [22]. There are some other reasons, such as internal strain/ internal pressure, and Mg deficiency, however that can also cause reduction in the $a$-parameter [23].

Analysis of the full width at half maximum (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. Therefore, the increased FWHM value of the (110) peak for the G-doped samples gives evidence of strain effects that have occurred due to the changes in the in-plane crystallinity from graphene doping [24].

In general, doping with other carbon sources does not affect the $c$-parameter, however, our refinement results show a slight variation in the $c$-parameter for these samples. Extension of the $c$-parameter has been reported by Zhang et al.[25] for a composite of graphene and MgB$_2$, and this was explained as one of the factors which is expected to enhance the critical temperature of MgB$_2$.

Figure 4.2 shows the Raman spectra for three doping levels, which were collected at room temperature in the range of 300 to 900 cm$^{-1}$. Raman spectra for MgB$_2$ which has a simple hexagonal structure in space group $P6/mmm$, feature four optical modes at the point of the Brillouin zone: a silent $B_{1g}$ mode (at 87.1 meV, $\sim 700$ cm$^{-1}$), the $E_{2g}$ Raman mode (at 74.5 meV, $\sim 600$ cm$^{-1}$), and the infrared active $E_{2u}$ (at 40.7 meV, $\sim 330$ cm$^{-1}$) and $A_{2u}$ (at 49.8 meV, $\sim 400$ cm$^{-1}$) modes [26].
Table 4.1 Lattice parameters and FWHM variation with the doping level.

<table>
<thead>
<tr>
<th>Graphene doping level (%)</th>
<th>Lattice parameter $a$ (Å)</th>
<th>Lattice parameter $c$ (Å)</th>
<th>$c/a$ ratio</th>
<th>FWHM (110) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.086(1)</td>
<td>3.526(1)</td>
<td>1.142</td>
<td>0.335</td>
</tr>
<tr>
<td>1</td>
<td>3.085(1)</td>
<td>3.527(1)</td>
<td>1.143</td>
<td>0.480</td>
</tr>
<tr>
<td>5</td>
<td>3.083(1)</td>
<td>3.524(1)</td>
<td>1.143</td>
<td>0.400</td>
</tr>
</tbody>
</table>

Figure 4.2: Raman spectra with Gaussian fitted $E_{2g}$ mode and phonon density of states (PDOS) for undoped and graphene doped MgB$_2$. The baselines have been subtracted from the patterns.
As chemical substitution can affect the crystal and electronic structure, as well as the degree of disorder, substitution can alter the phonon spectrum, by changing the phonon frequency and electron-phonon coupling strength [27]. There are three peaks observed for all the samples. The peak centred around 600 cm\(^{-1}\) arises from the \(E_{2g}\) phonon mode representing the in-plane B bond stretching, whereas the other two peaks represent the phonon density of states (PDOS) due to disorder.

Figure 4.3: SEM images of the un-doped (a, b), the 1% G-doped (c, d) and the 5% G-doped (e, f) MgB\(_2\) bulk samples respectively.
As evidenced by Figure 4.2, a slight Raman shift to lower frequency near 600 cm$^{-1}$ can be observed for the optimally doped sample (graphene 1%), which gives clear evidence of induced tensile strain in the 1% G-doped MgB$_2$ sample. As the doping level increases, however, the E$_{2g}$ phonon peak shifts to the higher frequency side, which indicates that the weakening of the electron-phonon coupling by carbon substitution dominates the induced tensile strain effect [27].

Figure 4.3 in panels (a), (c), and (e) shows SEM images of the undoped, 1% G-doped and 5% G-doped samples respectively. Panels (b), (d) and (f) in Figure 4.3 are SEM images of the same samples at a higher magnification. The grain structure and the morphology seem to be different in the un-doped and G-doped samples, as the latter crystals have grown under strain due to the C substitution effect. In terms of grain shape, there appear to be more bar grains in the G-doped samples, and most of those grains have merged together into big clusters. Therefore, based on the above observations, it seems that G-doped samples are highly dense and have more well-connected grains than the undoped sample.

### 4.3.2 Superconducting properties

Figure 4.4 shows the in-field J$_c$ performance at 5 and 20 K for the undoped and G-doped bulk samples. Critical current density curves for the G-doped samples show strong improvement over that of the un-doped sample at 5 K. At the optimal doping level (graphene 1 at. %), there is nearly 43 times improvement compared to the undoped sample at 8 T, 5 K. The critical current density at high fields near H$_{c2}$ is mainly governed by H$_{c2}$, hence higher H$_{c2}$ leads to a higher J$_c$ [28]. As reported by Li et al.[16], G-doped MgB$_2$ bulk samples prepared through the diffusion process showed high density of defects with fringes compared to the undoped sample. It also mentioned that
the presence of tensile strain that occurred due to the mismatch of the thermal expansions of graphene and MgB$_2$. Both these reasons helped to improve the flux pinning in MgB$_2$. Further, grain size reduction is always observed in the G-doped samples compared to the undoped sample, this also improves grain boundary pinning. This, together with the improved connectivity factor explains the reason why higher $J_c$ is observed in the 1 at. % G-doped sample at high fields. At zero field, 20 K, all samples showed quite high critical current density values of more than $4.1 \times 10^5$ A/cm$^2$. Critical current density degradation was not observed at zero field for doped samples, in fact, 1 at. % G-doped sample showed an improved zero field $J_c$ compared to the undoped sample. According to Matsushita et al.[29] there exists a strong correlation between connectivity and the self field $J_c$. Therefore, a better electrical connectivity, which means increased $A_F$ values, leads to higher $J_c$ values. Improvement in the critical current density both at low and high field can be attributed to improved connectivity and flux pinning due to graphene doping.

Figure 4.4: Critical current density as a function of applied magnetic field for undoped and G- doped MgB$_2$ bulk samples.
In order to compare the pinning behaviour of undoped and graphene doped samples, the variation of reduced flux pinning force \( f_p = F_p/F_{p,\text{max}} \) with reduced field \( h = H/H_{irr} \) at 20 K was studied.

According to the model proposed by Dew-Hughes, the general expression for the normalized pinning force density, \( f_p \), is given by Eq. (4.1)[30].

\[
f_p = F_p/F_{p,\text{max}} \propto h^p(1-h)^q
\]

where, the dimensionless parameters \( p \) and \( q \) depend on the specific characteristics of flux pinning in the superconductor, and \( h \) is the reduced magnetic field. To determine the value of \( H_{irr} \), a \( J_c \) criterion of \( 10^2 \text{A/cm}^2 \) was used.

As shown in Figure 4.5, the peak of the \( f_p \) curves occurs at \( h_{\text{peak}} \sim 2.5 - 2.7 \). One would expect that the surface pinning type to be obvious in the undoped sample, since the grain boundaries are identified as the main pinning mechanism [31, 32]. However, the curve with parameters \( p = 0.5 \) and \( q = 2 \) did not fit with the experimental data. Instead, the fitting procedure yields values of \( p \sim 1.6 \) and \( q \sim 5.3 \) for all the samples data.

![Figure 4.5: Normalized pinning force as a function of reduced field with fitted curves for the undoped and G- doped MgB2 bulk samples.](image)
The explanation of such pinning behaviour is still unclear, however, high q values were observed by other groups in MgB$_2$ [33]. The fitted results, however, could not be used to comment on the pinning mechanism.

In detailed analysis of the pinning mechanism in MgB$_2$, it is well established that the most important elementary interactions between vortices and pinning centres are the magnetic interaction and the core interaction.

Figure 4.6: Temperature dependence of the cross over field $B_{sb}$ of 1 at. % G-doped (above) and 5 at. % G-doped (below) MgB$_2$ bulk samples.
Magnetic interactions arise from the interaction of surfaces between superconducting and non-superconducting regions parallel to the applied field, whereas the core interaction arises from the coupling of the locally distorted superconducting properties with the periodic variation of the superconducting order parameter, which is dominant in MgB$_2$ [34]. The two mechanisms involved in core interaction are $\delta T_c$ pinning and $\delta l$ pinning. The $\delta T_c$ pinning is caused by the spatial variation of the Ginzburg-Landau (GL) coefficient $\alpha$, which is associated with disorder in the $T_c$, and the $\delta l$ pinning is caused by the variation of the charge-carrier mean free path $l$ near lattice defects. According to the model proposed by Qin et al., $\delta T_c$ is the most prominent pinning mechanism in pure MgB$_2$. Furthermore, the vortex solid region can be divided into three smaller regions, termed single vortex, small-bundle, and thermal fluctuation regions, depending on the applied magnetic field. The crossover field, $B_{sb}$, is defined as the field separating the single vortex regime from the regime where the vortices form small bundles, below which the $J_c$ is almost independent of the applied field. ($B_{sb}$ is taken as the field at which the $J_c$ drops by 5% compared to the $J_c$ at zero field.) The variation of $B_{sb}$ with reduced temperature ($t = T/T_c$) for $\delta T_c$ and $\delta l$ pinning is given by Eqs. (4.2) and (4.3), respectively:

$$B_{sb} = B_{sb}(0) \left[ \frac{(1-t^2)/(1+t^2)}{1} \right]^{2/3}$$

$$B_{sb} = B_{sb}(0) \left[ \frac{(1-t^2)/(1+t^2)}{1} \right]^2$$

As observed from Figure 4.6, the curve representing the $\delta T_c$ pinning is in good agreement with measured data for the 1% G-doped sample, while the data for the 5% G-doped sample shows a slight variation from $\delta T_c$ pinning behaviour, although it does not fit with $\delta l$ pinning. Generally, carbon doped MgB$_2$ obeys $\delta l$ pinning, owing to the increased scattering and hence,
the reduced charge-carrier mean free path \( l \) near lattice defects [7, 35]. This again indicates that graphene acts differently from other carbon sources when doped into the MgB\(_2\) matrix.

Table 4.2 summarizes the critical temperature, resistivity \( (\rho) \) at 40 K and 300 K, residual resistivity ratio \( (\text{RRR} = \rho_{300K}/\rho_{40K}) \), and active cross-section \( (A_F) \) of the pure and G-doped MgB\(_2\) bulk samples. Only a slight decrease in critical temperature is observed due to graphene doping. Even at the 5% doping level, \( T_c \) is decreased by just 1 K, which is not common with other carbon sources [3, 4].

Figure 4.7 shows the normal state resistivity of undoped and graphene doped MgB\(_2\) bulk samples. According to the classification of resistivity by Rowell, [21] all these samples lie in between the groups of low and intermediate resistivity samples, however, reduction of resistivity after doping is quite an extraordinary observation among carbon dopants.

It is very common to show increased resistivity for doped MgB\(_2\) samples, as the carbon reduces the electron mean free path, although the effective area factor appears to be more dominant in determining the resistivity of these MgB\(_2\) samples.

Table 4.2: Critical temperature \( (T_c) \), resistivity at 40 K and 300 K, residual resistivity ratio \( (\text{RRR}) \), and active cross-section \( (A_F) \) of undoped and G-doped MgB\(_2\) bulk samples.

<table>
<thead>
<tr>
<th>Graphene doping level (%)</th>
<th>( T_c ) (K)</th>
<th>( \rho ) (300K) (( \mu \Omega ) cm)</th>
<th>( \rho ) (40K) (( \mu \Omega ) cm)</th>
<th>( \text{RRR} )</th>
<th>( \Delta \rho ) (300K - 40K) (( \mu \Omega ) cm)</th>
<th>( A_F )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>38.9</td>
<td>37.52</td>
<td>10.17</td>
<td>3.68</td>
<td>27.34</td>
<td>0.1572</td>
</tr>
<tr>
<td>1</td>
<td>38.3</td>
<td>26.61</td>
<td>9.45</td>
<td>2.81</td>
<td>17.17</td>
<td>0.2504</td>
</tr>
<tr>
<td>5</td>
<td>37.9</td>
<td>30.36</td>
<td>10.43</td>
<td>2.87</td>
<td>19.60</td>
<td>0.2193</td>
</tr>
</tbody>
</table>
As can be seen from Table 4.2, the active cross-sectional area ($A_F$) has increased in the G-doped samples, which provides a clue to the reduction in resistivity. This improvement in the connectivity is confirmed by the SEM images presented in Figure 4.3. The improvement of $A_F$ for the 5% G-doped MgB$_2$, however, is less than for the 1% G-doped MgB$_2$, which explains the reduction of its $J_c$ performance, as the over-doping tends to reduce the intergrain connectivity. 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 value. The observed RRR values for the G-doped samples are smaller than for the pure sample, which is in a good agreement with the literature [21, 23].

![Figure 4.7: Variation of the normal state resistivity with temperature for undoped and G-doped MgB$_2$ bulk samples. Inset shows the variation of the normalized resistivity with temperature.](image-url)

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To analyse the temperature dependence of $\rho(T)$, the normalized normal-state resistivity values were fitted to the expression,

$$\rho(T) = \rho_0 + aT^n$$  \hspace{1cm} (4.4)

where, $\rho_0$ is the residual resistivity, $a$ is a parameter, and $n$ is the power law dependence of the resistivity [36].

According to the inset in Figure 4.6, the experimental data for undoped and graphene doped samples were well fitted by Eq (4.4) over the temperature range between $T_c$ and 300 K. For the undoped sample, the parameter values obtained from this fit are $\rho_0 = 0.2330 \, \mu\Omega \, \text{cm}$, $a = 4.19 \times 10^{-6} \, \mu\Omega \, \text{cm/K}^n$, and $n = 2.11$. The parameter values obtained for the 1% G-doped sample from this fit are $\rho_0 = 0.3158 \, \mu\Omega \, \text{cm}$, $a = 4.17 \times 10^{-6} \, \mu\Omega \, \text{cm/K}^n$, and $n = 2.09$. The parameter values obtained for the 5% G-doped sample from this fit are $\rho_0 = 0.2885 \, \mu\Omega \, \text{cm}$, $a = 5.86 \times 10^{-5} \, \mu\Omega \, \text{cm/K}^n$, and $n = 1.63$. The changes in the $n$ values obtained for our samples can be attributed to the disorder due to graphene doping, as the disorder reduces the value of $n$ [36].

The broadening of the resistive transition due to thermally activated flux flow (TAFF) in undoped and G-doped bulk samples was studied in order to determine the relationship between the flux-flow energy barrier, $U_0$, and the applied magnetic field. The main mechanism of flux creep or flux flow in MgB$_2$ is the thermal activation of flux line motion over the energy barrier $U_0$ of the pinning centres, and this is indicated by a broadening of the resistive transition [37]. This broadening (usually in the lower part of the resistive transition) is explained in terms of a dissipation of the energy arising from the motion of vortices. Therefore, it is considered that the resistance in the low resistance region depends mainly on thermally activated flux flow, which is given by Eq. (4.5):

$$\rho(T, B) = \rho_0 \exp[-U_0/k_BT]$$  \hspace{1cm} (4.5)
Where, $U_0$ is the flux-flow activation energy, which can be obtained from the slope of the linear part of the Arrhenius plot, $\rho_0$ is a field independent pre-exponential factor, and $k_B$ is Boltzmann’s constant [37].

Figure 4.8 shows the Arrhenius plots for the un-doped and G-doped samples. All curves show linear behaviour at low temperature, which indicates that the dependence of $U_0$ is

Figure 4.8: Arrhenius plots of the resistivity at different magnetic fields for undoped and G-doped MgB$_2$ bulk samples.
approximately linear at low temperature, and as the temperature goes up, it levels off at a field independent value which corresponds to the normal state resistivity [37].

As revealed in Figure 4.9, an enhanced value of $U_0$ can be seen for the graphene doped samples in the low field region, especially at the optimum doping level. The field dependences of $U_0$ for all samples showed a weak relationship with increasing field up to $B \approx 2.5$ T, where single-vortex pinning dominates. The un-doped sample follows the power law $U_0 \propto B^{-0.98}$, whereas the power for the 1% G-doped and 5% G-doped samples was around -0.75. The activation energy for all samples show a stronger field dependence at higher field, which is characteristic of collective creep [38]. The field dependence of $U_0$ for the undoped sample, however, follows the power law $U_0 \propto B^{-5.4}$, whereas the powers for the 1% G-doped and 5% G-doped samples were -2.14 and -2.81,
respectively, which indicates less field dependence of $U_0$ compared to the undoped sample.

### 4.4 Summary

A systematic study of the effects of graphene doping on the superconducting properties of MgB$_2$ has been conducted and improvements in superconducting properties, such as critical current density, and critical fields were observed due to graphene doping. Refinement results together with Raman analysis have shown that graphene doping leads to tensile strain in the MgB$_2$ lattice, which could be responsible for these improvements in superconducting properties. We found that $\delta T_c$ pinning is the flux pinning mechanism in graphene doped MgB$_2$. A noticeable enhancement in the flux-flow activation energy, $U_0$, was observed in graphene doped MgB$_2$ at low fields. All these improvements have had positive effects on the $J_c$ of the sample at the optimal doping level. Graphene is a novel and promising dopant for effectively enhancing the superconducting properties of MgB$_2$ without much reduction of $T_c$. Furthermore, we believe that graphene can also be used as a co-dopant for further enhancement in $J_c$ performance.
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4.5 References


Chapter 5: Effect of the Synthesis Route of Reduced Graphene Oxide on the Superconductivity of MgB$_2$

5.1 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 ($J_c$), and upper critical field ($H_{c2}$), and irreversibility field ($H_{irr}$). Compared to other low temperature superconductors, MgB$_2$’s high critical temperature allows it to be used in liquid-cryogen-free systems. However, its rapid drop in critical current with applied magnetic fields and its low critical fields exclude 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$_2$ [2-9]. 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 [10, 11].

There have been different procedures reported for the reduction of graphene oxide (GO), including chemical reduction, thermal annealing, microwave irradiation, etc [12-16]. Generally, GO refers to the exfoliated graphite oxide, existing in the form of single sheets or a few stacked 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 NaHSO₃, Na₂S·9H₂O, SOCl₂, Na₂S₂O₃, and SO₂ can be used as reducing agents to reduce GO in aqueous solutions [15]. The carbon to oxygen ratio of the end product, however, totally depends on the method of preparation and the degree of the reduction process [17]. Therefore, the aim of this study is to understand the effectiveness of the two-stage reduction process in reducing GO and the effects of these carbon additives on improving the superconducting properties of MgB₂.

5.2 Experimental details

5.2.1 Sample preparation

5.2.1.1 Preparation of rGO and rCCG:

rGO: GO was prepared and purified according to the modified Hummers method [18] and treated with thionyl chloride (SOCl₂) 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 powdered GO (500 mg) was treated with an excess of SOCl₂ in 1,2-dichloroethane for 2 hrs. After complete removal of the solvent and SOCl₂, the suspended rGO was washed with dichloromethane (DCM) and dried under vacuum overnight at 60°C to remove all traces of SOCl₂.

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 [14, 15]. Highly reduced CCG (rCCG) was obtained by treating an
aqueous dispersion of CCG (1.0 l, 0.5 mg/ml) 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 the rCCG (0.47 g). These fine agglomerates of rCCG (220 mg) were further treated with an excess quantity of SOCl₂ for two hours at 70°C [12]. The excess SOCl₂ was removed by washing with DCM and drying the powder under vacuum overnight, resulting in a quantitative yield of rCCG. Figure 5.1 illustrates the chemical route to the synthesis of the rGO and rCCG samples.

Figure 5.1: Schematic of the synthesis of rGO and rCCG
5.2.1.2 Fabrication of MgB₂ bulk samples

Graphene doped bulk samples were prepared by the diffusion method with crystalline boron powder (0.2 to 2.4 µm) 99.999%, Mg powder (99%, 352 mesh) and graphene produced different methods as precursors. Initially, boron was separately, mixed with rGO and rCCG powders in a motar according to the formula MgB₁.₉₉C₀.₀₁. Powders were then pressed into pellets 13 mm in diameter, and then inserted into a soft iron tube with the stoichiometric ratio of Mg to B, 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°Cmin⁻¹ under high purity argon (Ar 99.9%) gas.

5.2.2 Equipment used

The phase identification and crystal structure investigations were carried out at room temperature using an X-ray diffractometer (XRD, GBCMMA) with Cu-Kα radiation (λ = 1.54059 Å). X-ray photoelectron spectroscopy (XPS) was conducted using an ESCALAB220i-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 Kα (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 (TEM) was performed at using a JEOL 3000F field emission instrument located at the University of Sydney. TEM samples were prepared from solid samples by the dual beam focussed ion beam (FIB) technique (FEI xT Nova NanoLab 200 Nova
instrument, University of New South Wales) with thin slices lifted out onto a Quantifoil carbon support film.

The Raman scattering was measured using a confocal laser Raman spectrometer (HORIBA Jobin Yvon system) with a 100× microscope. The 632.8 nm line of a HeNe laser with power of about 20 mW was used for excitation.

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 from Bean’s model [19], using a Quantum Design physical properties measurement system (PPMS).

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, $\rho$, from Rowell’s model [20].
5.3 Results and Discussion

5.3.1 Characterization

The XRD analysis for GO, rCCG and rGO is shown in Figure 5.2. A typical broad peak near \( \theta = 9.86^\circ \), corresponding to a layer-to-layer distance (\( d \)-spacing) of \( \sim 0.896 \) nm was observed for the GO powder. A dramatic shift to higher \( \theta \) angles (\( \sim 25.56^\circ \) and \( 25.47^\circ \)) with decreased \( d \)-spacing of \( \sim 0.349 \) and 0.348 nm was observed for the rGO and rCCG samples respectively. This reduction of the \( d \)-spacing clearly indicates a better ordering of the two-dimensional structure [13].

![XRD patterns of GO, rCCG and rGO samples](image)

Figure 5.2: XRD patterns of GO, rCCG and rGO samples

The results from the XPS analysis are shown in Figure 5.3. The high resolution C1s spectra are compared between the GO sheets obtained before and after reduction. The GO spectrum, given in Figure 5.3(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 Figure 5.3(b), represents four environments corresponding to carbon atoms in different functional groups and assigned as C=C (sp², 284.4 eV), C–C (sp², 285.4 eV), C–O (286.3 eV), and C=O (carbonyl, 288.1 eV) [15, 21]. The C1s peaks in the XPS reveal that most 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 Figure 5.3(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 a result of the treatment with SOCl₂[22].

Figure 5.3: High resolution C1s spectra of (a) GO, (b) rGO and (c) rCCG
The atomic percentages from 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 gave 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 Figure 5.4, 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 [23]. FWHM values of the 110 peak are 0.3940, 0.3780, and 0.3420 for the samples of rCCG-doped, rGO-doped and undoped MgB$_2$ respectively. No significant shift in the (110) peak is visible as the doping level is very low, however, the increased FWHM values of the 110 peak of the doped samples compared with the undoped sample give evidence of increased lattice strain due to doping [23].

Figure 5.4: XRD patterns of undoped, rGO-doped and rCCG-doped MgB$_2$
Figure 5.5 in panels (a), (c), and (e) shows SEM images of the un-doped, 1% rCCG-doped and rGO-doped (e, f) MgB$_2$ samples.

Figure 5.5 in panels (a), (c), and (e) shows SEM images of the un-doped, 1% rCCG-doped and rGO-doped samples respectively. Panels (b), (d), and (f) in Figure 5.5 are SEM images of the same samples at a higher magnification. The images indicate a rather homogeneous grain structure, with the apparent grain size around 200 nm. The
grain structure and the morphology seem to be different in the undoped and G-doped samples, as in the latter case, most of the grains have merged together into big clusters. Therefore, based on the above observations, it seems that the G-doped samples are highly dense and have more well-connected grains than the undoped sample. The presence of a minor phase was also identified, particularly for the doped samples, and it appears as 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 (Figure 5.6). A low magnification image of the rGO-doped sample lifted out onto a Quantifoil carbon support film is shown in Figure 5.6(a). Regions of porosity (marked in Figure 5.6(a)) were not quantified, but appeared greater in the undoped MgB$_2$ sample than the other two. Contrast consistent with the presence of MgB$_2$ was obtained from high resolution images, such as the image in the inset in Figure 5.6(c), which shows lattice planes perpendicular to the c lattice direction. A significant difference between the undoped MgB$_2$, and the rCCG-doped and rGO-doped samples was evident in the mottled contrast, which is marked in Figure 5.6(b) and 5.6(f), consistent with a carbon containing coating that is distributed throughout the MgB$_2$. This contrast was absent in the undoped sample (Figure 5.6(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. Nevertheless, we believe that the presence of the reduced graphene that is evident in both the rCCG-doped and the rGO doped samples plays an important role in promoting grain connectivity and, thereby, improved superconducting properties.
CHAPTER 5: Effect of the synthesis route of reduced graphene oxide on the superconductivity of MgB$_2$

Figure 5.6: TEM images of MgB$_2$ samples prepared by focused ion beam milling: (a –c) rGO doped, (d) undoped, (e) and (f) rCCG doped samples. The inset to (c) shows a high magnification image of the rGO doped sample on a Quantifoil carbon support film.

Figure 5.7: Raman spectra with Gaussian fitted E$_{2g}$ mode and PDOS distortion of undoped, rGO-doped and rCCG-doped MgB$_2$
Raman studies were carried out on these samples at room temperature in the range of 300 to 1000 \text{cm}^{-1} and the Raman spectra are shown in Figure 5.7. Owing to the simple hexagonal structure (space group \textit{P}6/\textit{mmm}), four optical modes at the \textit{\Gamma} point of the Brillouin zone are predicted for \textit{MgB}_2: a silent \textit{B}_{1g} mode (at 87.1 meV, \approx 700 \text{cm}^{-1}), the \textit{E}_{2g} Raman mode (at 74.5 meV, \approx 600 \text{cm}^{-1}), the infrared active \textit{E}_{2u} (at 40.7 meV, \approx 330 \text{cm}^{-1}), and \textit{A}_{2u} (at 49.8 meV, \approx 400 \text{cm}^{-1}) [24]. There are two peaks in the measured range centred at about 600 \text{cm}^{-1} and 775 \text{cm}^{-1}. The low frequency Raman band is assigned to the \textit{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 [24, 25]. As revealed by Figure 5.7, a slight shift of the \textit{E}_{2g} band to the low frequency range can be observed in the doped samples when compared with the undoped sample, which gives evidence of induced tensile strain as a result of doping [10, 24]. The PDOS band becomes more prominent in the doped samples, indicating increased disorder due to doping [24].

\subsection*{5.3.2 Superconducting properties}

The magnetic critical current densities (\textit{J}_c) of undoped, rGO-doped, and rCCG-doped \textit{MgB}_2 bulk samples as a function of applied magnetic field are shown in Fig. 5.8. The \textit{J}_c performances of the doped samples were improved significantly under both low and high fields, even with only a small amount of doping (1 at. \%). At zero field and 20 K, \textit{J}_c values of the undoped, rGO-doped, and rCCG-doped samples were 4.1 \times 10^5 \text{Acm}^{-2}, 5.15 \times 10^5 \text{Acm}^{-2}, and 5.45 \times 10^5 \text{Acm}^{-2}, respectively. This is quite remarkable, as many carbon dopants have an adverse effect on \textit{J}_c in the low field region. According to Eisterer et al. [26], the connectivity is a major factor which governs the self-field \textit{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, in 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 sample. 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 [27].

Figure 5.8: In-field $J_c$ performance of undoped, rGO-doped and rCCG-doped MgB$_2$ bulk samples.
5.3.3 Resistivity analysis

Table 5.1 summarizes the critical temperature, residual resistivity ratio (RRR), difference between resistivities at 40 K and 300 K (Δρ), and active cross-section (A_F) for the undoped and doped MgB_2 bulk samples. Only a slight decrease in T_c, only 0.5 K, is observed due to doping. This is a remarkable feature in graphene doping, as most carbon sources are associated with a more T_c reduction [28], although, there are other parameters also affecting the T_c, such as doping level and sintering temperature. Therefore, the low level of doping and the sintering conditions would also have prevented much T_c reduction in this study.

The normal state resistivity variation with temperature is given in Figure 5.9 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. This reduction in resistivity, however, is in contrast with the general results of carbon doping, which tend to increase the resistivity after doping, due to increased interband and intraband scattering in the σ-bands [20].

Table 5.1: Critical temperature, residual resistivity ratio (RRR), difference between resistivity at 300 K and 40 K, and active cross-sectional area (A_F) of the undoped, rGO-doped and rCCG-doped MgB_2 bulk samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>T_c (K)</th>
<th>RRR</th>
<th>Δρ (300 K- 40 K) (µΩ cm)</th>
<th>A_F</th>
</tr>
</thead>
<tbody>
<tr>
<td>undoped</td>
<td>38.89</td>
<td>3.90</td>
<td>34.00</td>
<td>0.126</td>
</tr>
<tr>
<td>rGO-doped</td>
<td>38.39</td>
<td>3.32</td>
<td>29.98</td>
<td>0.143</td>
</tr>
<tr>
<td>rCCG-doped</td>
<td>38.56</td>
<td>3.45</td>
<td>21.28</td>
<td>0.202</td>
</tr>
</tbody>
</table>
In addition to that, as explained by Rowell et al. [20], the 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, although the rCCG-doped sample shows better improvement than the rGO-doped one. Increased electrical conductivity and higher amount of C presents in the sample, while the 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 [20, 29].

![Resistivity variation with temperature of undoped, rGO-doped and rCCG-doped MgB$_2$ bulk samples. Inset shows the variation of the normalized](image_url)
For further analysis of the temperature dependence of the normal state resistivity, normalised resistivity values were fitted with the following equation, \( \rho(T) = \rho_0 + aT^n \), where, \( \rho_0 \) is the residual resistivity, \( a \) is a parameter, and \( n \) is the power law dependence of the resistivity [30]. The inset of Figure 5.9 shows that the experimental data for undoped, rGO-doped 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 \( \rho_0 = 0.223 \mu\Omega \text{ cm}, a = 2.671 \times 10^{-6} \mu\Omega \text{ cm/K}^n \), and \( n = 2.19 \). The parameter values obtained for the rGO-doped sample from this fit are \( \rho_0 = 0.286 \mu\Omega \text{ cm}, a = 4.96 \times 10^{-6} \mu\Omega \text{ cm/K}^n \), and \( n = 2.07 \). The parameter values obtained for the rCCG-doped sample from this fit are \( \rho_0 = 0.251 \mu\Omega \text{ cm}, a = 2.87 \times 10^{-6} \mu\Omega \text{ cm/K}^n \), and \( n = 2.17 \). The changes in the \( n \) values can be attributed to the disorder due to doping, as the disorder reduces the value of \( n \) [30]. These fitted results, together with the RRR values, confirm the increased disorder due to doping. Therefore, the variations in the resistivity of the undoped and doped samples depend on the combined effect of the connectivity factor and the disorder.
5.4 Chapter summary

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 over a wide range of fields and very low resistivity for the rCCG-doped MgB$_2$ sample. Improvements in critical current density of all the doped samples are mainly attributed to improved intergrain connectivity, which is a salient feature in graphene doping. According to our results, rCCG made 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 $T_c$. 
5.5 References


CHAPTER 5: Effect of the synthesis route of reduced graphene oxide on the superconductivity of MgB$_2$


Chapter 6: Effects of Co-doping MgB$_2$ with Graphene and nano-SiC on the Superconducting Properties.

6.1 Introduction

Owing to the high critical temperature ($T_c$) of 40 K, intrinsically “weak-link” free grain boundaries, and low fabrication cost, MgB$_2$ is believed to be promising for replacing conventional low $T_c$ superconductors in many cryogen-free applications, such as magnetic resonance imaging, flywheels, high field magnets etc. For practical applications that require carrying large super-currents in the presence of magnetic field, improvement in the critical current density ($J_c$) has been the key research topic for MgB$_2$. So far, extensive research has been undertaken to enhance its superconducting properties, such as critical current density ($J_c$), upper critical field ($H_{c2}$) and irreversibility field ($H_{irr}$). A significant improvement in $J_c$–field dependence is one of the most important factors which would permit its usage in the industrial applications. Chemical doping can be identified as the simplest and cheapest way to improve the electronic structures of superconductors and their superconducting properties. In particular, carbon containing dopants, including silicon carbide (SiC), nano-carbon, carbon nanotubes (CNTs), hydrocarbons/carbohydrates, graphite, and graphene, are effective means to improve the $J_c$– field dependence and $H_{c2}$ [1-13].

Among all the dopants, SiC appears to be the most effective, as it results in a considerable density of microstructural defects, leading to superior improvement in the superconducting properties compared to the other carbon or carbon based dopants [1, 10]. As with in many carbon dopants, however, SiC too, has an adverse effect on $J_c$ in the low field region. On the other hand, graphene is one of the dopants which can
improve $J_c$ in the low field region, through improved inter-grain connectivity [14, 15]. In this work, we report our success in terms of a significant improvement in $J_c$ of MgB$_2$ in both low and high fields from co-doping with graphene and nano-SiC. Our findings pave the way for MgB$_2$ to be useful for both high and low field applications.

6.2 Experimental details

6.2.1 Fabrication of MgB$_2$ bulk samples

Graphene, SiC co-doped bulk samples were prepared via the diffusion method from crystalline boron powder (99.999%, 0.2 to 2.4 μm), Mg powder (99%, 352 mesh), SiC (99%, <30 nm) and highly reduced chemically converted graphene (rCCG) as precursors. This rCCG was obtained by excess reduction of an aqueous dispersion of chemically converted graphene, as reported by Dan Li et al. [16] using hydrazine at the refluxing temperature. The resulting rCCG agglomerates were dried completely and further treated with an excess quantity of thionyl chloride, as reported by Eda et al. [17] leading to further improvement in the electrical conductivity.

Initially, boron and graphene powders were mixed according to the weight ratio of MgB$_2$: graphene : SiC equals to 1: 0.025: x respectively, where x = 5 and 7.5 wt % SiC. The weight ratio of graphene was kept at a constant value of 2.5 wt % for co-doped samples, as this gave the optimum results in our previous work [14]. The powders, with the stoichiometric ratio of Mg to B, plus excess Mg to compensate for the loss of Mg during sintering, were then pressed into pellets 13 mm in diameter and inserted into a soft iron tube. The samples were sintered at 800°C for 10 hours in quartz tube at a heating rate of 5°C min$^{-1}$ under high purity argon (Ar 99.9%) gas.
CHAPTER 6: Effects of co-doping MgB₂ on the superconducting properties.

6.2.2 Equipment used

The phase identification and crystal structure investigations were carried out using an X-ray diffractometer (GBCMMA) with Cu-Kα radiation (λ = 1.5405 Å). 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 (TEM) was performed on powdered samples using a JEOL 2011 200 keV analytical instrument. The superconducting transition temperature, Tₐ, was determined from the AC susceptibility measurements, and the magnetic Jₐ was derived from the width of the magnetization loop using Bean’s model [18] using a physical properties measurement system (PPMS). The resistivity measurements were conducted using the standard dc four-probe technique under magnetic fields up to 13 T. The upper critical field (Hₑ₂) and the irreversibility field (Hᵢᵣ) 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 (Aₑ) was calculated from the resistivity, ρ, from Rowell’s model [19].
6.2 Results and Discussion

6.2.1 Characterization

According to the X-ray diffraction (XRD) patterns presented in Figure 6.1, the dominant phase within all the samples is MgB$_2$, however, Mg$_2$Si, unreacted SiC and Mg peaks also appear for the doped samples. As the SiC doping level increases, Mg$_2$Si peaks can be seen with more pronounced peak intensities [20]. Considerable shifts in the (110) peak to higher angles are observed in all doped samples. This can be attributed to some level of carbon substitution occurring at the B sites, resulting in a decrease in the $a$ lattice parameter [21, 22]. Trends in the full width at half maximum (FWHM) of

![Figure 6.1: X-ray diffraction patterns of the undoped, SiC doped, and co-doped MgB$_2$ bulk samples.](image-url)
the (110) MgB$_2$ peak (see Table 6.1), were also consistent with a decrease in nanocrystallite grain size due to an increase in the levels of either or both dopants and the degradation of crystallization caused by various types of lattice defects or intragranular precipitates [23, 24]. It can be noted that the $T_c$ reduction due to SiC doping and co-doping at the 5 wt% level, is not so significant. Further increases in SiC doping level, however, lead to higher levels of impurity phases, as evidenced by the XRD peaks associated with Mg$_2$Si and, unreacted SiC. The dopant incorporation into the MgB$_2$ structure in the form of carbon substituting for boron or in the form of additional impurities is believed to be responsible for the considerable observed drop in $T_c$ [24].

Figure 6.2 shows FESEM backscattered images of the doped and co-doped samples. There are four distinct greyscale intensities present in the images, where backscattered images show increasing brightness with atomic number. Region 1 is the darkest phase indicating that it has the lowest relative atomic number.

Table 6.1: Full width at half maximum (FWHM), critical temperature ($T_c$), resistivity at 40 K & 300 K, residual resistivity ratio (RRR), and active cross section ($A_F$) of undoped, SiC doped, and co-doped MgB$_2$ bulk samples.

<table>
<thead>
<tr>
<th>Doping level</th>
<th>$T_c$ (K)</th>
<th>$\rho$ (300K) ($\mu\Omega$ cm)</th>
<th>$\rho$ (40K) ($\mu\Omega$ cm)</th>
<th>RRR</th>
<th>$\Delta\rho$ (300K - 40K) ($\mu\Omega$ cm)</th>
<th>$A_F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC wt. (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>38.87</td>
<td>46.65</td>
<td>12.74</td>
<td>3.65</td>
<td>33.90</td>
<td>0.126</td>
</tr>
<tr>
<td>5</td>
<td>38.13</td>
<td>40.20</td>
<td>12.80</td>
<td>3.14</td>
<td>27.40</td>
<td>0.157</td>
</tr>
<tr>
<td>5 + G</td>
<td>38.12</td>
<td>38.18</td>
<td>12.40</td>
<td>3.07</td>
<td>25.78</td>
<td>0.167</td>
</tr>
<tr>
<td>7.5</td>
<td>36.10</td>
<td>83.66</td>
<td>52.12</td>
<td>1.60</td>
<td>31.54</td>
<td>0.136</td>
</tr>
<tr>
<td>7.5 + G</td>
<td>35.60</td>
<td>87.00</td>
<td>52.00</td>
<td>1.67</td>
<td>35.00</td>
<td>0.122</td>
</tr>
</tbody>
</table>
This phase is present at all levels of doping, and it increases with the amount of SiC and graphene doping. EDS analysis confirms the presence of Mg and B only in this phase (B-rich phase).

Region 2 is a lighter greyscale than region 1, indicating a higher relative atomic number. EDS confirms the presence of Mg and B only, however, with a higher Mg:B ratio responsible for the increased greyscale intensity. The area fraction of region 2 increases with the doping level and always shows a higher area fraction than region 1.

Figure 6.2: FESEM images of MgB2 bulk samples: (a) 5 wt% SiC doped, (b) co-doped 5 wt% SiC, (c) 7.5 wt% SiC doped, and (d) co-doped with 7.5 wt% SiC. (e) is an enlarged view of the area marked in (c).
CHAPTER 6: Effects of co-doping MgB$_2$ on the superconducting properties.

Region 3 is the most prominent phase in all the samples, however, the relative amount decreases with the level of doping. EDS analysis of this area confirms the presence of Mg, B, C, O and Si.

Region 4 is the brightest greyscale level indicating that this phase has the highest relative atomic mass. EDS analysis confirms the presence of Mg, B, C, O and Si, with a significantly higher Si and O concentration. The relative amount of this phase increases with the level of SiC doping.

From the above observations, it is clear that the addition of SiC contributes to the formation of Mg$_2$Si and B-rich phase, which has a favourable effect on improving flux pinning due to the formation of normal-superconducting interfaces [25]. Figure 6.2(e) is an enlarged view of the area circled in Figure 6.2(c), revealing the fine distribution of region 4 in the main MgB$_2$ matrix.

![Figure 6.3: TEM images obtained from the 5% SiC-graphene co-doped sample. (a) Low magnification TEM image with indicated selected area electron diffraction patterns obtained from region believed to contain graphene or graphite plus MgB$_2$ region, (b) bright filed contrast from MgB$_2$, indicating high defect densities, (c) high magnification contrast indicating the presence of significant amounts of amorphous carbon (taken from region over a hole in TEM support film).](image)
Preliminary transmission electron microscopy investigations were performed on powders prepared by the gentle grinding of bulk samples followed by deposition onto holey carbon support film. Here, the 5 wt% SiC co-doped sample was selected, due to its excellent $J_c$ performances at low fields. While further investigation of sectioned bulk samples is required to fully characterise the distributions of minor phases, including Mg$_2$Si, MgO and unreacted SiC, the TEM investigations revealed that the MgB$_2$ in the co-doped samples contained large concentrations of defects, typical of carbon doped specimens [13, 26]. Furthermore, excess carbon was also present, both in the form of graphene or graphite, and in terms of amorphous carbon. TEM results obtained from the co-doped sample containing 5 wt% SiC are shown in Figure 6.3. In the low magnification bright field image, Figure 6.3(a), the large circled area contains both MgB$_2$, as confirmed by the electron diffraction pattern obtained from the large circled region, and either graphene or a graphitic decomposition product of the original graphene additive, as indicated by the diffraction spots associated with the small circled region. Contrast from the MgB$_2$ regions revealed high densities of lattice defects and fringes (Figure 6.3(b)), which is characteristic of graphene doped MgB$_2$ samples [7]. These nanosized inclusions and lattice defects can serve as strong pinning centres to improve flux pinning. Further TEM investigations are required in order to distinguish the relative effects of carbon associated with the graphene doping and carbon associated with SiC decomposition on both the MgB$_2$ defect structures and the final microstructures of these samples. Figure 6.3(c) shows a different region of the sample, located over a hole in the sample support film. Contrast from amorphous carbon is indicated by the arrow (also confirmed by energy dispersive spectroscopy).
6.2.2 Critical temperature and resistivity analysis

The critical temperature and the temperature dependence of the resistivity for all samples were analysed, and the results are summarized in the Table 6.1. It can be noted that the $T_c$ reduction due to SiC doping and co-doping at the 5 wt% level is not so significant. Further increases in SiC doping level, however, lead to higher levels of impurity phases associated with Mg$_2$Si and, un-reacted SiC. The dopant incorporation into the MgB$_2$ structure in the form of carbon the substitution for boron or in the form of additional impurities is believed to be responsible for the considerable observed drop in $T_c$ [10, 24].

The samples with 5 wt% SiC doping and co-doping show very low resistivity values, similar to the resistivity of the undoped sample, although, with increasing the SiC doping level, a rapid increase in the resistivity was observed. The value of the active cross-sectional area ($A_F$) of the co-doped sample with 5wt% SiC shows a significant improvement compared to the other samples. Improvement in grain to grain connectivity was observed as one of the main benefits gained through graphene doping on MgB$_2$ [14, 15]. This may be either due to the presence of remanant graphene or graphitic decomposition products, as evidenced from TEM analysis, which could spread as a coating over the MgB$_2$ matrix making them more connected [15], or formation of MgB$_2$ on graphene sheets which results in more homogeneous structure with improved grain connectivity. According to Rowel et al. [12], factors such as porosity, density, and the presence of the impurity phases in the grains or on the grain boundaries need to be considered, as some factors affect the intergrain connectivity. Carbon substitution at boron sites increases the resistivity due to increased electron scattering and disorder. As evidenced by the FESEM images and XRD analysis, 5 wt% SiC doped and co-doped samples show better homogeneity, compared to 7.5 wt% SiC doped and co-doped...
samples, due to the low levels of secondary phases such as Mg$_2$Si and, unreacted SiC, which reflects better grain connectivity, as evidenced from the XRD analysis, FESEM images, and $A_F$ values.

With increasing the doping level, however, higher resistivities were observed in the doped samples, due to both inferior grain connectivity and the higher carbon substitution. The presence of non-superconducting phases such as Mg$_2$Si and, SiC tends to shorten the electron mean free path, $l$, resulting a reduced coherence length, $\xi$, according to the following Equation (6.1) [27].

\[
1/\xi = 1/l + 1/\xi_0 \quad (6.1)
\]

Where, $\xi_0$ is the coherence length for a perfectly pure superconductor.

The residual resistivity ratio (RRR), gives an indication of degradation of the crystallinity or increased disorder, and therefore, decreased values of RRR for the doped samples compared to the undoped one, reflect the effects of doping on the disorder of the samples [28].

**6.2.3 $J_c$ performance**

Figure 6.4 shows the in-field $J_c$ performance at 5 and 20 K for undoped, SiC doped, and co-doped bulk samples of MgB$_2$. All the doped samples show significant improvement of $J_c$ in terms of high field performance compared to the undoped sample. In particular, the $J_c$ curves for the co-doped samples show a significant improvement over the undoped and singly doped samples at both 5 and 20 K. At zero field, 20 K, the sample co-doped with graphene and 5 wt% SiC shows a quite high critical current density value of $5.77 \times 10^4$ A/cm$^2$, and it shows 40 % improvement compared to the undoped sample.
It should be noted that the reduction of $T_c$ for this sample is less than just 1 K compared to the undoped sample. The enhancement of $J_c$ in zero field, in this samples can mainly be attributed to improved connectivity [29]. Figure 6.5 presents the trend in $A_F$ as well as the trend in zero field $J_c$ for all samples in this study. A strong relationship between $A_F$ and zero field $J_c$ can be observed, as they follow a similar trend in both cases. According to the resistivity analysis, graphene and 5 wt% SiC co-doped sample exhibits the highest value of $A_F$, indicating excellent grain to grain connectivity. As can be seen from Figure 6.4, further increases in SiC adversely affect the zero field $J_c$. Reduction of the superconducting phase and inferior grain-to-grain connectivity can be considered as the reasons for such reduction in the $J_c$ performance [26, 30].

Figure 6.4: In-field $J_c$ performance at 20 K for undoped, SiC- doped and co-doped MgB$_2$ bulk samples. Inset shows the same at 5 K in the logarithmic scale.
CHAPTER 6: Effects of co-doping MgB$_2$ on the superconducting properties.

Figure 6.5: Comparison of the $A_F$ and the zero-field $J_c$ at 20 K of undoped, SiC- doped and co-doped MgB$_2$ bulk samples

Figure 6.6: Double logarithmic plot of $J_c$ of undoped, SiC- doped and co-doped MgB$_2$ bulk samples. Inset shows the $T_c$ variation of the same samples.
The sample doped with 5 wt% SiC also shows an enhancement in the zero-field $J_c$ performance, which is due to the improved $A_F$, as it has a strong correlation with the zero field $J_c$ performance. The sample co-doped with graphene and 7.5 wt% SiC, however, shows a remarkable value of $J_c$, $2.08 \times 10^4$ A/cm² at 5 K, 8 T, which is similar to the highest $J_c$ ever reported for bulk samples [6, 30]. This is nearly a 46 times improvement compared to the undoped sample. The high level of carbon substitution at boron sites and the presence of nanosize Mg₂Si impurity phase have significantly improved $J_c$ at high fields, through enhanced $H_{c2}$ and flux pinning [26, 27].

It is well-known that C doping adversely affects the $T_c$. Apart from that, a high level of doping can cause broadening of the transition, revealing quality differences between MgB₂ crystals in the sample [26]. The transition width $\Delta T_c$, is defined as the temperature difference between the onset value of the transition and the termination point of the transition. As can be seen from the inset of Figure 6.6, the transition is very sharp for the samples that are undoped, or have a low doping level of SiC (i.e. 5 wt%). This reveals the improved quality and the connectivity, which further strengthens the evidence obtained through the RRR and $A_F$ values derived from the resistivity data. A broader transition was observed for the 7.5 wt % SiC doped sample, indicating the high level of disorder in each sample. Based on the details in Figure 6.6, the co-doped 5 wt% SiC sample shows the best performance in terms of $J_c$ at low field, which mainly depends on the improved grain connectivity. The performance of $J_c$ at low field of the undoped sample is also significantly high, although it drops rapidly at high fields. The samples with high doping levels (7.5 wt% SiC) show steadily improved performance at high fields owing to high disorder, although they show poor performance in low field. Furthermore, those two samples clearly exhibit power law exponents in the small-
bundle region, $J_c \propto B^{-\alpha}$, revealing better high field performance due to improved pinning force.

### 6.2.4 $H_{c2}$ and $H_{irr}$

![Normalized temperature dependence of upper critical field $H_{c2}$ and irreversibility field $H_{irr}$ for undoped, SiC-doped and co-doped MgB$_2$ bulk samples](image)

Figure 6.7: Normalized temperature dependence of upper critical field $H_{c2}$ (a), and the irreversibility field, $H_{irr}$ (b) for the undoped, SiC-doped and co-doped MgB$_2$ bulk samples.
CHAPTER 6: Effects of co-doping MgB$_2$ on the superconducting properties.

The temperature dependence of upper critical ($H_{c2}$) and irreversibility ($H_{irr}$) fields are shown in Figure 6.7. It can be seen that, both $H_{c2}$ and $H_{irr}$ have increased dramatically in all doped samples compared to the undoped sample. $H_{c2}$ can be expressed according to the equation (6.2).

$$H_{c2} = \frac{\Phi_0}{2\pi\mu_0\xi^2}$$

(6.2)

Where $\xi$ is the coherence length, $\Phi_0$ is the superconducting flux quantum, and $\mu_0$ is the magnetic permeability. Therefore, $H_{c2}$ increases as $\xi$ decreases. The scattering results shorten mean free path, which causes a reduction in $\xi$, thereby resulting an increased $H_{c2}$ [27]. Degradation of the crystallinity is directly linked to the lattice disorder and precipitates, which affects the intraband scattering.

The best improvement in $J_c$ at high fields was observed in the co-doped sample with 7.5 wt% SiC. Such improvement in critical fields was gained due to several reasons, such as, (i) C substitution on B sites, which results in an increase in intraband scattering, (ii) the formation of nano-domain structure, and (iii) formation of Mg$_2$Si impurity phase [26]. The enhancement of $H_{irr}$ with increasing doping level can be related to the increased FWHM of the (110) peak which represents the introduced disorder due to doping, in the $ab$- plane [27]. This increase in the FWHM is strongly related to the electron scattering at grain boundaries, which is dependent on the purity of the sample. Therefore, higher critical fields obtained for the 7.5 wt % SiC -doped and co-doped can be related to the increased disorder due to doping.
6.3 Chapter summary

The effects of co-doping with graphene and nano-SiC with MgB$_2$ were systematically investigated. A significant improvement of critical current density at low fields was observed in the sample co-doped with graphene and 5 wt% SiC, with only a small depression in the $T_c$. It revealed that the inter-grain connectivity was the dominant factor governing the performance of $J_c$ at zero-field while high $H_{c2}$ and flux pinning governs the $J_c$ performance at high field in graphene and nano-SiC with MgB$_2$ bulk samples.

By combining the advantage of strong flux pinning gained through SiC doping and good connectivity gained through graphene doping, the co-doping is a better approach that can be used to improve the superconducting properties in both low fields and high fields.
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Chapter 7: Effects of Graphene Oxide Doping on the Superconducting Properties of MgB$_2$

7.1 Introduction:

Since the discovery of superconductivity in MgB$_2$ [1], extensive research has been undertaken to enhance its superconducting properties, such as critical current density ($J_c$), upper critical field ($H_{c2}$), and irreversibility field ($H_{irr}$). MgB$_2$ exhibits much higher critical temperature ($T_c$) compared to other low temperature superconductors, allowing it to be used in liquid-cryogen-free systems [2]. Nevertheless, its rapid drop in critical current under applied magnetic field and low critical fields exclude it from many industrial applications where a high $J_c$ under high magnetic field is required. Many studies have shown that, carbon containing dopants, including nanosize carbon (nano-C), silicon carbide (SiC), carbon nanotubes (CNTs), hydrocarbons/carbohydrates, graphite, and graphene are effective means to enhance the field dependence of $J_c$ and $H_{c2}$ of MgB$_2$. Most carbon dopants, however, adversely affect $T_c$ and the low field $J_c$ performance [2-10].

Among these dopants, graphene has been 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 [8, 9]. Although, the high cost of pure graphene renders it impractical for large-scale applications. Furthermore, the re-stacking of graphene sheets during the process results in an inevitable performance penalty. An easier way is to employ graphene oxide, which is typically monolayer in nature. It is used to make the
composite material, and the final structure is then thermally reduced to prevent the aggregation of graphene sheets [11]. Apart from the facile synthesis method, graphene oxide has the advantages of cost and suitability for mass production, which make it sensible candidate for industrial scale applications [12]. Since the agglomeration of additives has been always the main problem the solid state mixing, it is a great challenge to achieve a homogeneous dispersion of the nano-dopants in the matrix material. Although available well-dispersed aqueous colloids of exfoliated GO allow homogeneous mixing of dopant in MgB$_2$, these aqueous solutions degrade the performance of MgB$_2$. In almost all of the most promising solution processing methods, toluene is considered to be an integral component, even though it adversely affect $T_c$ [13]. In the case of graphene or graphene oxide processing, however, toluene exhibits no advantage, mainly because of the inevitable restacking of graphene or graphene oxide layers during the process. Tetrahydrofuran (THF) has been used as an organic solvent to disperse GO sheets, as it can satisfy all of the requirements of a suitable organic solvent that can prevent the oxidation of boron or Mg powder [14], while simultaneously dispersing GO. Dispersing GO in THF, however, is not regarded a straightforward task as it typically involves agglomeration of GO particles [15]. Yet, employing extremely large GO sheets in our case not only led to effective dispersion of GO sheets in THF, but also resulted in achieving graphene oxide liquid crystals in the THF. In this chapter, we demonstrate that processibility of GO dispersions in organic solvents can be further exploited to fabricate doped MgB$_2$ samples which can satisfy all of the above-mentioned requirements and exhibit extremely good low- and high-field performance.
7.2 Experimental details

7.2.1 Preparing the GO suspension

The experimental set-up and procedure for the synthesis of graphene oxide (GO) were based on our previously reported synthesis methods [12, 16, 17]. In a typical synthesis run, 1 g of expandable graphite flakes (Asbury Graphite Mills, US) was thermally expanded at 1050 °C for 15 s. The as-prepared worm-like expanded graphite (EG) was then used as the starting material for the production of GO. 1 g of EG and 200 ml of sulphuric acid (H₂SO₄, 98%, Merck) were mixed in a three-neck flask. Next, 10 g of KMnO₄ was added to the mixture while stirring. The mixture was then stirred for 24 h. Next, 200 ml of de-ionized (DI) water and 50 ml of H₂O₂ were added to the mixture. The resulting mixture was washed using HCL solution (9 : 1 vol water : HCl) three times, then centrifuged again and washed with de-ionized water until the pH of the solution reached a value of 5 to 6. The obtained GO sheets were then diluted using DI water (2 mg/ml) to obtain a liquid crystalline (LC) dispersion of GO in water. Anisotropic LC GO dispersions in THF were prepared after the collection of the material by centrifugation and removal of water supernatant. Water was replaced by an equal volume of THF by extraction of water via repeated centrifugation and washing with THF.

7.2.2 Doping GO into MgB₂

GO-doped bulk samples were prepared via the diffusion method from crystalline boron powder (0.2 to 2.4 µm 99.999%), Mg powder (99%, 352 mesh), and a homogeneous
suspension of GO in THF, as precursors. Initially, the boron and the GO solution were mixed by hand milling according to the formula MgB_{2-x}C_x, where x = 0, 1, 2, 3, and 4 at % GO in THF solution. Powders were then dried at 25°C under vacuum conditions for about 2 hours, which allows coating of B by the carbon from the solution. These powders were later pressed, into pellets 13 mm in diameter and inserted into a soft iron tube in the stoichiometric ratio of Mg to B, plus 20% excess Mg to compensate for the loss of Mg during sintering. The samples were sintered at 800°C for 10 hours in a quartz tube at a heating rate of 5°Cmin^{-1} under high purity argon (Ar 99.9%) gas.

7.2.3 Equipment used

The phase identification and crystal structure investigations were carried out at room temperature using an X-ray diffractometer (GBCMMA) with Cu-Kα radiation (λ = 1.54059 Å).

The Raman scattering was measured using a confocal laser Raman spectrometer (HORIBA Jobin Yvon system) with a 100× microscope. The 632.8 nm line of a HeNe laser with power of about 20 mW was used for excitation.

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.

The GO samples were investigated using an Asylum research MFP-3D Atomic Force Microscope (AFM). Images were collected using AC (tapping) mode imaging under ambient conditions with Mmasch NSC15 tipsSi_3N_4 coated silicon cantilevers.

Transmission electron microscopy (TEM) was performed on powdered using a JEOL 2011 200 keV analytical instrument.
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 [18], using a Quantum Design physical properties measurement system (PPMS). 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, $\rho$, from Rowell’s model [19].

7.3 Results and discussion

7.3.1 Characterization

Figure 7.1: a) SEM, b) AFM, c) high resolution TEM micrographs of as-prepared GO sheets and d) polarized optical micrograph of LC graphene oxide dispersion in THF.
The as-prepared GO samples were analyzed by SEM, AFM, and TEM investigations. AFM studies in conjunction with electron microscopy confirmed the monolayer nature of the as-prepared GO dispersions. Our as-prepared GO dispersions mostly consisted of monolayer GO sheets with sheet sizes of approximately 50 µm, as evidenced by SEM and AFM (Figure 7.1). Large-area graphene sheets are highly desirable, mainly because of the much lower amount of defects on their basal planes, arising from the lower amount of non-stoichiometric oxygen, which also makes the dispersion of GO in THF possible.

![Figure 7.2: XRD patterns for undoped and GO-doped MgB₂](image)

The XRD measurements were performed on the ground MgB₂ pellets. According to the XRD patterns presented in Figure 7.2, all peaks can be indexed to MgB₂ lines corresponding to the hexagonal P6/mmm structure. Although the GO contains nearly 35% oxygen, the peak near 62° which represents MgO (220) can hardly be seen in the
XRD patterns of all samples. The diffusivity of Mg is much faster than the diffusivity of MgO, therefore, there is a lesser possibility that oxygen contamination from the precursor material will occur, as happens in the in-situ method. In the diffusion process, Mg is diffused into boron pellet during sintering. An increased trend towards more MgO is observed with increasing the doping level (see Table 7.1). The lattice parameters, $a$ and $c$, the ratio of $c$ to $a$, the grain size, the strain, the full width at half maximum (FWHM) of the peak (110), and the MgO level calculated from the XRD patterns are shown in Table 7.1.

Figure 7.3 shows an enlarged view of the XRD patterns close to the angle of 60° to give clear evidence on the peak shift that occurs due to GO doping. The refinement results indicate that both the $a$-axis and the $c$-axis parameters vary with increasing GO doping level.

![Figure 7.3: Enlarged view of XRD patterns near 60° of undoped and GO-doped MgB$_2$](image)
CHAPTER 7: Effects of graphene oxide doping on the superconducting properties of MgB$_2$

Table 7.1: Lattice constants, $c/a$, grain size, strain, FWHM of the (110) peak, MgO intensity ratio of undoped and GO-doped MgB$_2$ bulk samples.

<table>
<thead>
<tr>
<th>sample</th>
<th>Lattice constants</th>
<th>$c/a$</th>
<th>Grain size</th>
<th>Strain</th>
<th>FWHM</th>
<th>$I_{MgO}(220)/I_{MgB_2}(101)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$a$ (Å)</td>
<td>$c$ (Å)</td>
<td>(nm)</td>
<td>(%)</td>
<td>(110) (˚)</td>
<td>(%)</td>
</tr>
<tr>
<td>Undoped</td>
<td>3.0844</td>
<td>3.5260</td>
<td>1.1427</td>
<td>195.70</td>
<td>0.1336</td>
<td>0.3420</td>
</tr>
<tr>
<td>1% GO-doped</td>
<td>3.0841</td>
<td>3.5307</td>
<td>1.1435</td>
<td>167.40</td>
<td>0.2025</td>
<td>0.4000</td>
</tr>
<tr>
<td>2% GO-doped</td>
<td>3.0843</td>
<td>3.5316</td>
<td>1.1441</td>
<td>159.70</td>
<td>0.2045</td>
<td>0.4200</td>
</tr>
<tr>
<td>3% GO-doped</td>
<td>3.0826</td>
<td>3.5283</td>
<td>1.1442</td>
<td>128.90</td>
<td>0.2038</td>
<td>0.4580</td>
</tr>
<tr>
<td>4% GO-doped</td>
<td>3.0792</td>
<td>3.5235</td>
<td>1.1443</td>
<td>125.40</td>
<td>0.1794</td>
<td>0.4580</td>
</tr>
</tbody>
</table>

Increases in the $c/a$ ratio and a considerable shift in the (110) peak to higher angles with increasing doping level, indicate that some amount of carbon substitution has occurred in the B sites [20, 21]. Among the various XRD peaks, the full width half maximum (FWHM) of the (110) peak is related to the in-plane crystallinity, while the FWHM of the (002) peak reflects the out-of-plane disorder [22]. According to the Williamson-Hall, the strain and the grain size affect the FWHM value [23]. FWHM values, therefore, provide considerable information on crystallite size and strain in the sample. The increased trend of the FWHM values obtained from the GO-doped samples compared to the undoped sample give evidence of reduced grain size and increased lattice strain due to doping [21]. In fact, the calculated results on grain size and lattice strain from a Williamson–Hall plot [23], like the experimental results given in table 7.1, which show a similar trend, would strengthen the above evidences even more.
The microstructural investigations were carried out by FESEM on powders of undoped and 2 at% GO doped MgB$_2$ bulk samples, and the results are presented in Figure 7.4. Figure 7.4(a, c, e) contains images of the undoped MgB$_2$ sample at several magnifications while Figure 7.4(b, d, f) presents images of the 2 at % GO doped MgB$_2$
sample, respectively. Here, 2 at % GO-doped sample was selected, due to its excellent \( J_c \) performances at low fields. The grain structure and the morphology seem to be different in the un-doped and GO-doped samples, as the latter crystals have grown under strain due to the C substitution effect. In terms of grain shape, there appear to be more separate spherical grains in the undoped sample, unlike in the GO-doped samples, where it seems that the grains have merged together into big clusters. This gives visible evidence on improved inter-grain connectivity in the GO-doped sample as it seems to have more well-connected grains than the un-doped sample.

![Raman spectra with Gaussian fitted \( E_{2g} \) mode and PDOS distortion of undoped, 2 at % and 4 at % GO-doped MgB\(_2\)](image)

Figure 7.5: Raman spectra with Gaussian fitted \( E_{2g} \) mode and PDOS distortion of undoped, 2 at % and 4 at % GO-doped MgB\(_2\)
GO-doped bulk samples in the range of 450 to 950 cm\(^{-1}\). There are two peaks visible in the measured range centred at about 610 cm\(^{-1}\) and 785 cm\(^{-1}\), similar to those reported in the literature. The low frequency Raman band is assigned to the Raman active E\(_{2g}\) mode which is strongly coupled to the electronic conduction \(\sigma\)-band, while the high frequency band is attributed to the phonon density of states (PDOS) due to disorder [24].

Figure 7.5 shows the room temperature Raman spectra for the undoped, 2 at \% and 4 at \%. Since doping affects the electron-phonon coupling intensity and crystal distortion, this will influence the Raman shift and the line width (FWHM) of the Raman scattering. As evidenced by Figure 7.5, both the E\(_{2g}\) peak and PDOS peak of the GO-doped sample have slightly shifted to higher frequency, indicating that the band structure of the MgB\(_2\) shows a higher phonon vibration frequency due to carbon substitution at boron sites as a result of doping. Furthermore, the intensity of the PDOS distortion has become more pronounced in the doped sample, which implies increased disorder compared to the undoped sample [25].

### 7.3.2 Critical temperature and resistivity analysis

The normal state resistivity variation with the temperature of the undoped and GO-doped MgB\(_2\) bulk samples is given in Figure 7.6. Table 7.2 presents the critical temperature, resistivity at 300 K and 40 K, the residual resistivity ratio (RRR = \(\rho_{300K}/\rho_{40K}\)), and the active cross-sectional area (\(A_F\)) of the undoped and GO-doped MgB\(_2\) bulk samples. From these results, the GO-doped samples exhibit low resistivities. Instead of showing increased resistivity owing to increased inter-band and intra-band scattering in the \(\sigma\)-bands [19], the GO-doped samples exhibit low resistivities. This behaviour can be explained by the counteracting effects of improved connectivity and
increased disorder due to GO doping. The stable dispersion of GO mono layers in THF solution (Figure 7.1) has resulted in a homogeneous dispersion of the dopant in the MgB$_2$ matrix, meaning that the intergrain connectivity has been improved due to the absence of agglomerations of dopant. With increasing doping level, however, the resistivity tends to rise, owing to increased band scattering due to higher C substitution. The increased $A_F$ values (Table 2) reveal that the connectivity has been improved due to GO doping, which is further evidenced by the FESEM images. The RRR, i.e., the ratio of the resistivity at 300 K to that at 40 K, reflects the degree of disorder, where higher electron scattering leads to a low RRR value [26].

Figure 7.6: Variation of the normal state resistivity with temperature for the undoped and GO-doped MgB$_2$ bulk samples.
The fact that the RRR values for the GO-doped samples are smaller than that of the undoped sample again proves the increased disorder, which is in agreement with the results revealed in XRD and Raman analysis. It should be mentioned that GO doping appears to have another benefit, as it does not greatly affect on $T_c$. For example, only 1.2 K reduction was observed for the 2 at% GO doped sample, which shows a significant enhancement of $J_c$ at both low and high fields.

Table 7.2: Critical temperature ($T_c$), resistivity at 300 K & 40 K, residual resistivity ratio (RRR) and active cross-sectional area ($A_F$) of the undoped and GO- doped MgB$_2$ bulk samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_c$ (K)</th>
<th>$\rho$ (300 K) ($\mu\Omega$ cm)</th>
<th>$\rho$ (40 K) ($\mu\Omega$ cm)</th>
<th>RRR</th>
<th>$A_F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>undoped</td>
<td>38.9</td>
<td>47.02</td>
<td>12.74</td>
<td>3.69</td>
<td>0.125</td>
</tr>
<tr>
<td>1% GO-doped</td>
<td>38.1</td>
<td>33.62</td>
<td>11.85</td>
<td>2.83</td>
<td>0.197</td>
</tr>
<tr>
<td>2% GO-doped</td>
<td>37.7</td>
<td>21.4</td>
<td>9.08</td>
<td>2.35</td>
<td>0.349</td>
</tr>
<tr>
<td>3% GO-doped</td>
<td>37.3</td>
<td>28.39</td>
<td>12.93</td>
<td>2.19</td>
<td>0.278</td>
</tr>
<tr>
<td>4% GO-doped</td>
<td>37.2</td>
<td>30.84</td>
<td>14.33</td>
<td>2.15</td>
<td>0.26</td>
</tr>
</tbody>
</table>

7.3.3 Superconducting properties

The in-field $J_c$ performances of the undoped and GO-doped MgB$_2$ bulk samples as a function of applied magnetic field are shown in Figure 7.7. The $J_c$ performances of all doped samples have improved significantly under both low and high fields, showing considerably better results compared to the performances with other carbon dopants and doping levels. (see Table 7.3 for a comparison). The sample with 2 at% GO showed a $J_c$ that was 27 times higher compared to that of the undoped sample at 5 K, 8 T, with a
### Chapter 7: Effects of graphene oxide doping on the superconducting properties of MgB$_2$

Table 7.3: Comparison of $J_c$ values from this study with others reported so far.

<table>
<thead>
<tr>
<th>Dopant</th>
<th>Method</th>
<th>$J_c$ 20K self-field ($\times 10^5$) A/cm$^2$</th>
<th>$J_c$ 5K 8T ($\times 10^4$) A/cm$^2$</th>
<th>Type of Boron</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>This study</td>
<td>Diffusion</td>
<td>6.3</td>
<td>1.18</td>
<td>Crystalline (99.999%)</td>
<td></td>
</tr>
<tr>
<td>n-SiC (10 wt.% doped)</td>
<td>In situ</td>
<td>6.0</td>
<td>2.0</td>
<td>Amorphous (99%)</td>
<td>APL * 81 3419</td>
</tr>
<tr>
<td>n-SiC (10 wt.% doped)</td>
<td>In situ</td>
<td>1.0</td>
<td>&lt; 1.0</td>
<td>Amorphous (95-97%)</td>
<td>SST * 24 045013</td>
</tr>
<tr>
<td>Adipic (5 wt.% acid doped)</td>
<td>In situ</td>
<td>na</td>
<td>3.0</td>
<td>na</td>
<td>SST 22 015016</td>
</tr>
<tr>
<td>Nano C (5 mol % doped)</td>
<td>In situ</td>
<td>4.0</td>
<td>1.8</td>
<td>Amorphous (99%)</td>
<td>SST 19 596</td>
</tr>
<tr>
<td>Multi CNT (20 mol % doped)</td>
<td>In situ</td>
<td>3.0</td>
<td>1.0</td>
<td>Amorphous (99%)</td>
<td>APL 83 4996</td>
</tr>
<tr>
<td>Malic acid (30 wt.% doped)</td>
<td>In situ</td>
<td>4.0</td>
<td>2.6</td>
<td>Amorphous (99%)</td>
<td>APL 89 142505</td>
</tr>
<tr>
<td>Graphite (10 mol % doped)</td>
<td>In situ</td>
<td>6.0</td>
<td>&lt; 1.0</td>
<td>Amorphous (99%)</td>
<td>JAP * 102 093910</td>
</tr>
<tr>
<td>n-SiC (10 wt.% doped)</td>
<td>Diffusion</td>
<td>6.0</td>
<td>1.2</td>
<td>Crystalline (99.999%)</td>
<td>APL 94 042510</td>
</tr>
<tr>
<td>n-SiC (10wt.% doped)</td>
<td>In situ</td>
<td>2.0</td>
<td>na</td>
<td>Amorphous (99%)</td>
<td>SST 22 085015</td>
</tr>
<tr>
<td>SiCl$_4$ (10 wt.% doped)</td>
<td>In situ</td>
<td>5.0</td>
<td>3.0</td>
<td>Amorphous (99%)</td>
<td>PRB 481 224514</td>
</tr>
<tr>
<td>Sugar (10 wt.% doped)</td>
<td>In situ</td>
<td>na</td>
<td>2.0</td>
<td>Amorphous (99%)</td>
<td>Sst 21 015005</td>
</tr>
<tr>
<td>CNT (2.5 mol % doped)</td>
<td>In situ</td>
<td>4.5</td>
<td>1</td>
<td>Amorphous (99.99%)</td>
<td>SST20 L12</td>
</tr>
<tr>
<td>CNT (10 mol % doped)</td>
<td>In situ</td>
<td>2.7</td>
<td>2.0</td>
<td>Amorphous (99%)</td>
<td>SST 19 L5</td>
</tr>
<tr>
<td>n- carbon (10 mol % doped)</td>
<td>In situ</td>
<td>3.5</td>
<td>1.5</td>
<td>Amorphous (99%)</td>
<td>SST 19 596</td>
</tr>
<tr>
<td>10 wt.% polycarbosilane</td>
<td>In situ</td>
<td>20</td>
<td>na</td>
<td>Amorphous (99.999%)</td>
<td>SST 19 68</td>
</tr>
</tbody>
</table>

slight drop in $T_c$ of just 1.2 K. At the same time, it showed a $J_c$ of $6.35 \times 10^5$ A/cm$^2$ at 20 K at zero field, which was increased by a factor of 1.5 compared to the undoped $J_c$ value. This is very significant, as most carbon dopants tend to reduce $J_c$ at low fields [4, 6]. Although there is a continuous improvement in $J_c$ at low fields with increasing doping level, low-field $J_c$ starts to show a slight reduction when the doping level exceeds 2 at%. According to Matsushita et al. [27], a strong correlation exists between the connectivity and the self-field $J_c$. Therefore, better electrical connectivity, which means higher $A_F$ values, leads to higher self-field $J_c$ values.

As can be seen from Table 7.2, the doping level of 2 at% shows the highest $A_F$ value, which is therefore consistent with the low-field $J_c$ improvement. The high-field $J_c$
performance, however, is greatly affected by $H_{c2}$, and the flux pinning mechanism hence improves with increasing doping level. Furthermore, an increased amount of MgO was detected with increasing GO doping level through XRD analysis. These MgO precipitates also act as effective pinning centres, which would therefore improve the high field performance [28]. Moreover, increases in $H_{\text{irr}}$, the FWHM value of the (110) peak, and strain, as well as decreased grain size indicate enhanced grain boundary pinning due to GO doping.

Broadening of the resistive transition due to thermally activated flux flow (TAFF) in undoped and GO-doped bulk samples was studied in order to determine the relationship between the flux-flow energy barrier, $U_0$, and the applied magnetic field. The main mechanism of flux creep or flux flow in MgB$_2$ is the thermal activation of flux line motion over the energy barrier $U_0$ of the pinning centres, and this is indicated by a broadening of the resistive transition [29]. This broadening (usually in the lower part of the resistive transition) is explained in terms of a dissipation of the energy arising from the motion of vortices. Therefore, it is considered that the resistance in the low resistance region depends mainly on thermally activated flux flow, which is given by the Equation (7.1):

$$\rho(T, B) = \rho_0 \exp\left[-\frac{U_0}{k_BT}\right]$$

(7.1)

Here, $U_0$ is the flux-flow activation energy, which can be obtained from the slope of the linear part of the Arrhenius plot, $\rho_0$ is a field independent pre-exponential factor, and $k_B$ is Boltzmann’s constant [29].
The plot is linear at low temperatures, which indicates that the dependence of $U_0$ is approximately linear at low temperatures, and as the temperature goes up, the plot levels off at a field independent value which corresponds to the normal state resistivity [29].

As revealed in Figure 7.8, increasing values of $U_0$ in the high field region can be seen for the GO-doped samples as the doping level increases. This demonstrates improved pinning at high field, which help us to understand the better performance of $J_c$ at high fields. The field dependences of $U_0$ for all samples showed a weak relationship with increasing field up to $B \approx 2.5$ T, where single-vortex pinning dominates. The activation energy for all samples shows a stronger field dependence at higher field, which is characteristic of collective creep [30]. The field dependence of $U_0$ for the undoped sample, however, follows the power law $U_0 \propto B^{-5.4}$, whereas the powers for the 1 at %,
2 at %, and 3 at % of GO-doped samples were -3.0, -2.41, and -2.58, respectively, which indicates less field dependence of \( U_0 \) compared to the undoped sample.

The temperature dependences of the upper critical (\( H_{c2} \)) and irreversibility (\( H_{irr} \)) fields are shown in Figure 7.9. It can be seen that, both \( H_{c2} \) and, \( H_{irr} \) have increased dramatically in all GO-doped samples, compared to the undoped sample. According to the equation \( H_{c2} = \Phi_0/(2\pi\mu_0\xi^2) \), where \( \xi \) is the coherence length, \( \Phi_0 \) is the superconducting flux quantum, and \( \mu_0 \) is the magnetic permeability, \( H_{c2} \) is determined by \( \xi \). \( H_{c2} \) increases as \( \xi \) decreases. Increased scattering results in a shorter mean free path, which causes a reduction in \( \xi \), thereby resulting in an increased \( H_{c2} \) [22]. As can be seen from the Figure 7.9, a noticeable improvement can be seen with increasing doping level up to 2% GO, however, the further enhancement is that not pronounced with the higher doping levels. This may be due to the near saturation of carbon substitution for boron at this sintering condition. Therefore, further addition of the dopant may not be effective in improving the critical fields as earlier. However,
contribute pinning centres and thereby improves the irreversibility field. This is the reason for the observed continual improvement of $J_c$ at high magnetic fields in the figure 7.7, within the doping level discussed in this work.

### 7.4 Chapter summary

In summary, we have systematically studied the effects of GO doping on the microstructure, crystallinity, resistivity, and critical current density of MgB$_2$ bulk samples. Increased lattice strain and disorder were observed due to the carbon substitution effect. Substantially enhanced $J_c$ properties under high fields and improved critical fields were observed in the GO doped samples with only a slight depression of $T_c$. A remarkable enhancement of the zero-field $J_c$ was obtained for the 2 at % GO doped sample, owing to improved intergrain connectivity. Increased the flux-flow activation energy was observed both at low and high magnetic fields. The field dependences of $U_0$ for all samples showed a strong relationship at high field, however, the rate of field dependency was decreased with doping level increasing. This indicates the improved pinning due to doping.

This study will open up new opportunities for large-scale manufacturing of nano-doped MgB$_2$ through a solution route with a cheap additive -GO, which is capable of improving both low and high field $J_c$. 
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7.5 References


Chapter 8: Research Summary and Suggestions for Further Improvement

8.1 Research summary

With improving the critical current density of MgB₂ under both low and high magnetic fields being the main concern, this thesis has systematically investigated the effects of graphene (G) and graphene oxide (GO) doping and co-doping with SiC and G on the superconductivity of MgB₂. High supercurrents were observed in the samples with good connectivity and large distortion. The suitability of MgB₂ in applications largely depends on \( J_c \) performance both at high and low fields.

Only a slight drop in the critical temperature (\( T_c \)), can be observed in G-doped MgB₂. It is worth mentioning that carbon can influence \( T_c \) in two ways. In the first, carbon substitutes on boron sites in the MgB₂ matrix, while in the second, carbon can stay as an inclusion in the MgB₂ lattice or a grain boundary impurity, giving rise to the impurity scattering effect. Graphene and graphene oxide are considered to be rather stable at high temperature due to the strong C-C bonds, therefore, they would release a comparatively small amount of carbon preferentially from the edges. A considerable amount of carbon, however, is believed to remain as an impurity phase. Apart from that, high purity of the boron source and quite long sintering conditions at 800°C have led to improved crystallinity, resulting in higher \( T_c \).

The intergrain connectivity was the main factor, which was affected positively due to G-doping. A direct measure of this can be calculated from the active cross sectional area (\( A_F \)), based on the resistivity data analysis. Increased \( A_F \) values are evidence for the
improved intergrain connection. The scanning electron microscope (SEM) images give the visible evidence of well-formed MgB$_2$ grains compared to the undoped samples. The grain structure and the morphology seem to be different in the undoped and G-doped samples, as the latter crystals have grown under strain due to the C substitution effect. In terms of grain shape, there appear to be more separate grains in the undoped samples, unlike in the doped samples, where it seems that the grains have merged together into big clusters. The improvement of the current density ($J_c$) was observed in the G-doped samples compared to the undoped one prepared under the same conditions, which is due to the improved $A_F$ and upper critical field ($H_{c2}$). The improvement in the $J_c$ performance at zero field was remarkable in the G-doped MgB$_2$, as most of the carbon dopants have adverse effects on this. A reduction in resistivity, improved critical fields, and improved flux-flow activation energy were observed in the G-doped samples compared with the undoped sample.

In the study of the synthesis methods for graphene, the two-step method provides more effective reduction over the single step reduction method. This effectiveness was evidenced in the graphene characterization based on the X-ray photoelectron spectroscopy (XPS) data. Reduction using hydrazine and further reduction using thionyl chloride solution reduced the oxygen level by half compared to the oxygen present after the single step method. Considerable improvement of the critical current density ($J_c$) was observed in the chemically converted graphene (rCCG)-doped samples compared to the reduced graphene oxide (rGO)-doped and undoped samples prepared under the same conditions, which is due to the improved $A_F$ and $H_{c2}$. Furthermore, transmission electron microscope (TEM) images reveal the presence of mottled contrast consistent with a carbon-containing coating, which distributed throughout the G-doped MgB$_2$. 
Furthermore, the sample slices prepared by dual beam focussed ion beam milling gave visible evidence of reduction in the appearance of pores in the G-doped samples.

Co-doped MgB\textsubscript{2} samples showed excellent J\textsubscript{c} performance both at high and low fields. The improved J\textsubscript{c} performance at zero field showed a similar trend with increased A\textsubscript{F}. The T\textsubscript{c} reduction at a low level of SiC doping was not pronounced, but with higher level of SiC doping there was a significant reduction in T\textsubscript{c} with increasing doping level. As evidenced by the TEM images, the presence of remnant carbon in the form of graphene or graphitic product and amorphous carbon was revealed in the co-doped samples. The improved intergrain connectivity, increased H\textsubscript{c2}, and strong pinning resulted in excellent J\textsubscript{c} performance both at high and low fields for the SiC and G co-doped samples with a low doping level of SiC.

The novel technique that was used to obtain a dispersion of GO in an organic solvent, tetrahydrofuran (THF) resulted in a stable, homogeneous dispersion, as the dopant can easily be dispersed into the MgB\textsubscript{2} matrix. This resulted in enhanced effectiveness of GO as a dopant. The SEM images reveal the improved intergrain connectivity in the GO-doped samples, as they seems to have more well-connected grains than the undoped samples. Improvement of the critical current density (J\textsubscript{c}) was observed in GO-doped samples compared to the undoped one prepared under the same conditions. The improvement in the J\textsubscript{c} performance at zero field was remarkable in GO-doped MgB\textsubscript{2} as other carbon dopants adversely affect this. This improvement is mainly attributed to the improvement in intergrain connectivity. Although the J\textsubscript{c} performance at high-fields was improved in G-doped, the improvement is not very significant compared with other carbon sources. A significant enhancement of the J\textsubscript{c} performance at high-fields was
observed, however, in GO-doped MgB$_2$ bulk samples, compared to the high-field performances of other carbon dopants. This is very remarkable, as doping with GO can lead to enhancement the $J_c$ performance both at high and low fields.

The $J_c$ performance at high fields is mainly governed by $H_{c2}$ and the flux pinning, and therefore, it improves with increasing doping level. A reduction in resistivity originating from the better connectivity in the GO-doped samples was observed compared with the undoped sample. Increased resistivity, however, was observed at higher doping levels, owing to increased disorder due to doping. This was further evidenced by the residual resistivity ratio (RRR) compared to the undoped samples in each case. In the GO-doped samples, the reduction in RRR is large compared with the G-doped sample, which indicates a higher degree of disorder in the GO-doped samples.

Improved upper critical field ($H_{c2}$) and irreversibility field ($H_{irr}$) were observed in all the doped samples compared to the undoped samples. This is mainly attributed to the impurity scattering, which causes a reduction in the coherence length, $\xi$, and enhanced pinning due to doping. This enhanced pinning in the GO-doped samples was also confirmed with the enhanced flux flow activation energy, especially at high fields.

The best $J_c$ results presented in this thesis were summarized and presented in the Table 8.1.

Table 8.1: Comparison of the best $J_c$ values from this thesis

<table>
<thead>
<tr>
<th>Dopant</th>
<th>$J_c$ 20K self-field ($\times 10^5$) A/cm$^2$</th>
<th>$J_c$ 5K 8T ($\times 10^4$) A/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped</td>
<td>4.1</td>
<td>0.014</td>
</tr>
<tr>
<td>1 at% G-doped</td>
<td>5.4</td>
<td>0.59</td>
</tr>
<tr>
<td>5 wt% SiC Co-doped</td>
<td>5.7</td>
<td>0.65</td>
</tr>
<tr>
<td>7.5 wt% SiC Co-doped</td>
<td>3.4</td>
<td>2.05</td>
</tr>
<tr>
<td>2 at% GO-doped</td>
<td>6.3</td>
<td>1.18</td>
</tr>
<tr>
<td>4 at% GO-doped</td>
<td>5.4</td>
<td>1.78</td>
</tr>
</tbody>
</table>
8.2 Suggestions for further improvement

Further studies on the fabrication of GO-doped MgB$_2$ the form of wire/tapes will be beneficial for the practical applications. The products made through the diffusion method are benefited with the high density. Presently, investigations are carrying out to employ the same technique to fabricate wires, however, the fabrication of long-length wires is still an unresolved issue. The use of combination of in-situ and ex-situ techniques is also a better suggestion to improve the density of the products.

In addition, the use of high energy milling technique is another suggestion to improve the density of the final product. The use of this technique results in the small grain size and improved the reactivity of boron. Both those facts lead to enhance the $J_c$ performance. Nevertheless, the use of tetrahydroforun (THF) as a milling medium will be impossible due to its high rate of evaporation. Therefore, further studies on the chemical synthesis procedure together with the milling process will be beneficial in order to find another suitable organic solvent.
Publications:


Manuscripts under preparation:


