3.1 Introduction

Nearly nine decades have been passed since the discovery of phenomenon ‘superconductivity’ [1], when a material ‘magnesium diboride’ (MgB$_2$) was discovered, exhibiting a superconducting drop at about 39K [2]. During such big span of time, the field of superconductivity has seen a remarkable progress, may it be the development of superconducting materials or the technology which made it possible to place it at the platform of applications. But still it has to cover a long distance to reach a stage of common day to day applications. Many low T$_c$ as well as high T$_c$ superconductors such as simple metals, alloys like Nb based compounds, organic superconductors, molecular superconductors, bismuth oxide based superconductors, borocarbides [3, 4] and cuprate superconductors etc. have been developed and successively experimented for their enhanced performance in possible applications. The MgB$_2$ superconductor also attracted enormous interest in its synthesis and simultaneously been tried for improvement in its superconducting properties. Since its discovery many efforts have been taken to improve the properties of MgB$_2$ from application point of view as it exhibits impressive properties such as high critical temperature amongst intermetallic superconductors, weak link free grain coupling, comparatively large coherence length, low material cost, simple crystal structure etc. Amongst these, one of the primitive efforts has been made in the direction of doping the B sites by carbon [5, 6]. The improved upper critical field and critical current density with small decrement in T$_c$, MgB$_2$ has emerged as an interesting material due to doping of carbon. High upper critical field values of H$_c^2$(0 K)$|| \sim 70$T and the H$_c^2$(0K)$\perp > 40$T were derived from quasiclassic Usadel equations for the two-band superconductors in the dirty limit [7]. The untextured carbon doped MgB$_2$ filaments fabricated by CVD technique showed high H$_c^2$ values of the order of
The study of carbon doped MgB₂ thin films prepared by different techniques gave a record high value of \( H_{c2}(4.2 \, \text{K}) > 50 \, \text{T} \). Thus idea of partial replacement of boron by carbon is expected and proved to be excellent alternative for enhancing the \( H_{c2} \) of MgB₂ superconductor and taking it a step further towards its applications. But one of the main pillars in the application point of view, for superconductors is the fabrication of the superconducting materials itself. Variety of different in situ and ex situ synthesis techniques such as hot isostatic pressing, sputtering, chemical vapor deposition, pulsed laser deposition, powder in tube technique, solid state diffusion for bulk as well as thin films etc. were developed for the range of superconductors depending upon, what application is to be targeted. Thus various superconducting materials were researched and fabricated into different forms. This made altogether a range of techniques and necessary experience available, for the synthesis of MgB₂ superconductors. But in fact the synthesis of MgB₂ superconductor turned up to be tedious due to extreme properties of its constituent elements Mg and B. Mg has a very high vapor pressure and a low melting point \( (650^\circ \text{C}) \) while B has a large melting point \( (2076^\circ \text{C}) \). The problem also gets added up due to strong affinity of Mg towards oxygen to form highly stable MgO phase. This result into the loss of Mg due to evaporation and formation of MgO before the reaction between Mg and B actually take place. The high vapor pressure of Mg also renders the samples porous and brittle. This behavior of Mg warrants a synthesis process which will take care of Mg losses by evaporation as well as its oxidation which degrades the formation of MgB₂ phase. To tackle this, Akimitsu et al synthesized the MgB₂ samples by hot isostatic pressing using Mg as well as amorphous B powder and heat treated at 973K. Since then MgB₂, more often has been synthesized by employing a rather convoluted high pressure or high vacuum technique which not only lead to a rather complicated synthesis
procedure but also render it least economical. At the same time high vacuum reduces the decomposition temperature drastically [11, 12]. So there is a need to develop the technique which will synthesize MgB$_2$ samples at ambient atmosphere along with the possible doping of carbon.

In this line, the low cost synthesis of MgB$_2$ thin film by electrodeposition [13, 14], electocrystallization [15-17] and electrophoretic [18] techniques have already been worked out. In continuation with these efforts, the present chapter entails the efforts carried out for the economical, least complicated and innovative preparation of carbon doped MgB$_2$ superconducting bulk samples under ambient atmosphere. The superconducting MgB$_2$ samples have been synthesized by solid state route and structurally characterized with the help of x-ray diffraction technique and the effect of carbon doping on lattice parameter is studied. Finally the electronic transport and magnetization measurements have been carried out to study the superconducting properties.

### 3.2 Experimental details

The carbon doped MgB$_2$ samples were synthesized by solid state reaction between 99 % pure magnesium (size ~ 100 µm) and 99% pure amorphous boron powder (size ~ 200 mesh). The amorphous carbon powder (size ~ 300 mesh) was used as a source for carbon doping as well as for creating carbon environment. The ingredient Mg and B powders were taken in various B:Mg ratios corresponding to 2:1 (1:0.5), 1:1 and 1:1.5 and then thoroughly grinded and mixed for about 3 hrs in agate mortar for homogenization and the samples were referred to as M1, M2 and M3 respectively. After homogenization, the blend of Mg and B were palletized under a pressure of 10 ton/cm$^2$. Each pellet thus formed was placed along with carbon powder in a graphite crucible packed with another crucible and
fired at 900 °C for 3hrs in a box furnace. The sample thus obtained after heat treatment were brushed out to remove the excess carbon from their surface. All the samples were characterized for their structural and phase confirmation by x-ray diffraction (XRD) studies carried out using Phillips-3710 powder diffractometer in the diffraction angle (2θ) range of 20-80°. The growth morphology of the samples was studied using scanning electron microscope (SEM) JEOL JSM 6360. The buffering action of carbon was studied by carrying out the thermogravimetry analysis (TGA) and differential thermal analysis (DTA) of carbon powder and unreacted blend of Mg and B in the temperature range of room temperature to 1000°C under air environment with the temperature ramp of 10°C/min using Transanalytical instrument SDT 2960. The superconducting behavior of samples was confirmed by four probe resistivity technique using Keithley (2001) multimeter and a constant current source (model 224). The contacts were made by air drying the silver paste. The samples were cooled up to 10 K with Janis make helium close cycle cryogenic refrigerator (model 22). The superconducting properties were also confirmed through magnetic susceptibility measurement using SQUID magnetometer (MPMS 2 Quantum Design).

3.3 Results and discussion
3.3.1 X-ray diffraction studies

The XRD studies of the samples after heat treatment were carried out to confirm MgB$_2$ phase formation and the variations in the lattice parameter due to carbon doping. Fig. 3.1(a-c) shows the XRD patterns of the samples M1, M2 and M3 with varying magnesium content (B:Mg ratio of 2:1, 1:1 and 1:1.5 respectively), prepared by the proposed carbon assisted synthesis.
Fig. 3.1: X-ray diffraction pattern of sample (a) M1, (b) M2 and (c) M3 with B to Mg ratio of 2:1, 1:1, 1:1.5 respectively.
process at ambient pressure conditions without using any inert gas
environment. Though the sample M1 is prepared with stoichiometric B to Mg
ratio of 2:1, peaks corresponding to unreacted B, Mg deficient phases of MgB₄
along with some MgB₂ phases are observed (Fig. 3.1(a)). The presence of
unreacted B and Mg deficient phases of MgB₄ suggests that there may be lack
of sufficient amount of Mg in the sample required for the formation of pure
MgB₂ phase. The deficiency of Mg may obviously be created because of Mg
losses, possibly due to its high vapor pressure, as no pressurized or inert
argon environment was employed. The process of formation of pure MgB₂
requires melting of Mg at around 650°C and then its diffusion in B to form
MgB₂ [19, 20, 21]. As a result, the boron site may act as a nucleation centre for
the formation of MgB₂ and increase in Mg concentration will help to improve
the phase formation of MgB₂. This is due to the fact that as the amount of Mg
increases, it will surround B more efficiently to increase the nucleation
centers for MgB₂ phase formation, resulting in the reduction of unreacted
phases of boron as revealed in the XRD patterns (fig. 3.1 (b) and (c)) for the
samples M2 and M3 with increased magnesium content. As the amount of Mg
approaches the optimum ratio of B to Mg, there might be sufficient nucleation
centers for continuous formation of MgB₂ phase which causes the observed
enhancement in intensity of MgB₂ peaks. Hence, optimum formation of MgB₂
phase occurred with B:Mg ratio of 1:1.5 (Fig: 3.1 (c)). The absence of
magnesium deficient phases of MgB₄ and complete disappearance of B or
B₂O₃ phases indicates that all the B content present in the sample is used up
for the formation of MgB₂ along with the traces of MgB₂C₂. Here, the sample
was sufficiently covered by carbon powder which reacts with oxygen to form
CO₂ or CO gas, thus consuming major amount of O₂ from the immediate
environment, rendering almost oxygen free ambiance favorable for Mg and B
reaction to form MgB₂ phase as depicted in the XRD pattern of the samples.
Only traces of $O_2$ reach the sample to form oxides of Mg or B. Thus, this layer of carbon powder over sample acts as a screening layer for $O_2$ and prevents the sample from being oxidized, and thus creating virtual inert environment there by assisting the reaction between Mg and B to form MgB$_2$ as against the reaction between Mg and O to form MgO.

The sample was prepared and studied for the extent of carbon doping. The carbon doping effects have been studied by considering the shift in the diffraction angle corresponding to (110) peak [22, 23]. Such observed shift in diffraction angle of (110) peak is shown in Fig. 3.2.

**Fig. 3.2:** Shift in the diffraction angle of (110) peak observed to be consistent in three reproduced carbon doped M3 samples marked as M3 (a) (solid triangle), M3 (b) (solid circles) and M3 (c) (solid square).
To confirm the consistency of this shift observed in the diffraction angle, the sample M3 was replicated many times and the shifts observed in case of three representative samples is presented in Fig 3.2 ((a), (b) and (c)). The peak shifts from 58.8° towards higher angle of 60.3° resulting in considerable decrement in ‘d’ value. This indicates the decrease in in-plane lattice parameter from 3.086 to 3.061 Å for M3 sample. This decrease in the a-axis lattice parameter is due to the substitution of in-plane boron sites by carbon [7, 24]. This is in agreement with the results reported by Avdeev et al. [23]. As per their results, the (c/a) ratio for the carbon doped MgB2 lattice varies with amount of carbon doping and is empirically given by relation (3.1),

\[
C(x) = 7.5 \times \Delta \left( \frac{c}{a} \right) \quad \text{........................................}(3.1)
\]

where, \( C(x) \) is the amount of carbon doping and \( \Delta (c/a) \) is the difference between the aspect ratio of carbon doped MgB2 unit cell and standard (i.e. undoped) unit cell [2]. In the present investigation, this well known relation is used to estimate the carbon content in the optimized sample. The carbon substitution in sample can be expressed as in the formula MgB\(_{1.8}\)C\(_{0.2}\). The presence of carbon in MgB\(_2\) was also confirmed from EDAX measurements of the sample as shown in the Fig 3.3.
3.3.2 Morphological studies

The SEM micrographs of the samples M1, M2 and M3 were recorded and are shown in Fig. 3.4 (a), (b) and (c). The SEM image of sample M1 shows a complete discrete morphology devoid of any significant signature of grain growth. On the other hand, sample M2 shows a distinct signature of grain growth but with discontinuous formation of island like grains in the sample which depicts localized grain growth. In contrast, the micrograph of sample M3 shows noticeable continuous and cannibalistic growth morphology. Thus, it is observed that as the amount of Mg increases the morphology of samples becomes increasingly continuous and compact. This is in support to our argument that as the amount of Mg increases, the nucleation centers for Mg and B reaction increases to form MgB$_2$ thereby resulting in the formation of continuous and compact grain morphology. The more enlarged SEM image of the M3 sample is shown in Fig. 3.4 (d) which further confirms the compactness of grains.

Fig. 3.3: EDAX pattern for sample M3 revealing the presence of carbon.
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Fig. 3.4: SEM image of (a) Sample M1 showing discrete morphology (1000X) (b) Magnesium deficient sample M2 showing discontinuous morphology (500X) (c) Well developed and continuous morphology of sample M3 with optimum Mg concentration. (500X) (d) SEM image of sample M3 at magnification 1000X.
3.3.3 Role of carbon

Carbon plays a crucial role of generating a virtual inert environment and favorable conditions for the synthesis of MgB$_2$ in the proposed work. This can be clearly understood by looking at the thermal analysis curves for the powders of carbon as well as blend of Mg and B. The differential thermal analysis (DTA) and thermogravimetry analysis (TGA) for the powders of carbon as well as blend of Mg and B was carried out in air for the temperature ranging from room temperature to 1000°C with temperature ramp of 10°C/min. The corresponding plots are as shown in Fig. 3.5 and Fig. 3.6 respectively. The inset of Fig 3.6 shows the TGA plot of Mg and B blend. From figures it is seen that a sharp exothermic peak is accompanied by a complete weight loss of carbon powder. This clearly indicates the oxidation of carbon powder that gets liberated in the form of CO$_2$ or CO gas which results in complete weight loss in TGA curves. As shown in Fig. 3.5 the oxidation reaction commences at about 450°C and its rate increases exponentially up to 501°C beyond which it shoots up; thereafter giving rise to highly intense peak at 505°C with the peak height or temperature difference of about 8.49°C/mg. On the other hand the thermal analysis curves for the blend of Mg and B shows an exothermic peak accompanied by the gain in the weight. This effect reveals the oxidation reaction of blend Mg and B. The oxidation reaction commences at 585°C giving an exothermic peak at 587°C with the peak height or temperature difference of just 3.09°C/mg which is less than 50 % of that for carbon powder. Moreover, the oxidation reaction of carbon powder occurs quite earlier as compared to that for the blend of Mg and B. This depicts the fact that the oxidation reaction of carbon powder occurs early and is highly preferred and vigorous as compared to that of Mg and B blend. Considering this fact, if the pellet of Mg and B blend is sufficiently covered by carbon powder, it is quite possible that the oxygen from the surrounding
atmosphere will first react with carbon shield providing almost oxygen free environment around the pellet. This will create a virtual inert environment which will help Mg to react with B instead of reacting with oxygen and form MgB$_2$ phase. The formation of exceptionally better MgB$_2$ phase in M3 sample as depicted by XRD pattern proves that the excess Mg along with the usage of carbon serves the said purpose and assists the formation of MgB$_2$.

![Differential thermal analysis (DTA) of carbon powder and unreacted Mg and B blend.](image)

**Fig. 3.5:** Differential thermal analysis (DTA) of carbon powder and unreacted Mg and B blend.
Fig. 3.6: Thermogravimetry analysis (TGA) of carbon powder. Inset shows the TGA for unreacted Mg and B blend.

The highly exothermic reaction of carbon powder may also provide sufficient localized temperature for further enhancement in the synthesis of MgB$_2$. Thus, it is clear that the carbon environment not only provides the buffering against oxygen but also acts as a source of carbon doping in MgB$_2$ and assists the synthesis of carbon doped MgB$_2$ samples.
3.3.4 Microwave response

The analysis of samples using microwave throws light on the surface resistance of the conducting material and presents a comparatively precise tool to test surface quality of samples. The surface resistance measurement using microwave response provide results, which is averaged over entire surface of sample. It gets influenced by any sort of defect, like presence of foreign particle or different phases that may be formed on the sample surface during the whole course of synthesis or post synthesis processing. Taking into consideration of these stringent testing possibilities the synthesized bulk samples were tested for their surface quality by studying their response to microwave exposure.

Of the various techniques, present resonant techniques are the most widely used for the surface resistance measurements. The technique employed the use of some form of resonating structure of which sample is either part and contributes to conduction loss or placed inside the resonating structure perturbing the electromagnetic field and thus producing additional losses. In the present investigation overlay technique was used to probe the sample surface. Here Cu stripline deposited on alumina substrate were used to obtain the microwave response from the sample. The corresponding dimension for the Cu stripline was 25 X 0.63 X 0.63 mm on the alumina substrate of 1 X 1 inch dimension. The stripline showed the characteristic impedance of 50 Ω. The microwave response was obtained by considering the microwave absorbance or $S_{21}$ (Forward Transmission Coefficient (Gain or loss)) parameter for the as synthesized bulk MgB$_2$ samples at room temperature. This was achieved by using N5230A PNA-L vector network analyzer with range 10 MHz to 20 GHz.
Fig. 3.7: Experimental arrangements for measurement of microwave absorbance ($S_{21}$) parameter of MgB$_2$ sample.

Fig. 3.8: Microwave absorbance ($S_{21}$) parameter measured for bare stripline
The special platform required for the measurements was fabricated to mount the stripline and to fit the launchers at both end of the stripline. The schematic diagram of the set up is as shown in Fig. 3.7. Fig. 3.8 shows microwave response of bare copper stripline on alumina plate recorded in the frequency range 10 MHz to 20 GHz. It is seen that the frequency range from 3-8GHz corresponds to the flat region with minimum microwave absorbance. At rest of the frequencies there is absorbance due to other losses. Hence the range of 3-8 GHz was selected for further microwave absorbance measurements of the sample.

Fig. 3.9: Microwave response for the samples M1, M2 and M3 in the frequency range of 3-7.5 GHz.

The room temperature microwave response of the sample M1, M2 and M3 are as shown in the Fig. 3.9. Fig. 3.9 shows that sample M1 do not show any
microwave response. This is because sample M1 doesn’t consist of MgB$_2$ phase as shown in the XRD pattern for the sample M1. As the amount of Mg was increased, there was enhanced phase formation observed in the sample M2 and M3. This is reflected in the microwave absorptions by these samples. It can be observed that the absorption for sample M3 is comparatively larger than that for sample M2. This indicates that sample M3 consists of increased MgB$_2$ phase formation along with improved connectivity. This is in confirmation with the SEM images for the samples M2 and M3 respectively.

The surface resistance for the samples M2 and M3 was determined from the microwave response. It was observed that the surface resistance for sample M2 came out to be 0.12 Ω and that for sample M3 was found to be 0.10 Ω at room temperature.

Fig. 3.10: Microwave response for the M3 (a) before polishing and M3 (b) after polishing.
The decrease in surface resistance for sample M3 as compared to M2 again confirms the improved continuity and grain connectivity in the sample as depicted by the SEM images for these samples.

**Fig. 3.11:** Depth profiling for the sample M3.

Further the as synthesized sample consists of a layer of carbon on the surface covering the sample. This is because the samples were synthesized in the carbon environment. Hence the sample was required to be polished in order to remove the upper layer on the samples. To determine the depth of layer, the samples were subjected to microwaves to check their response. Fig. 3.10 shows the microwave response for the sample M3 before polishing M3 (a) and after polishing M3 (b). Since MgB$_2$ is more or less metallic it gives a good conducting nature and will absorb the microwaves on the surface, but the absorption will be prohibited if it is covered by carbon layer. Hence the
sample was polished till the constant sustained microwave response was observed and the depth was measured using surface profiler. The depth obtained by surface profiler at which the sample showed considerable microwave absorption came out to be 13.5 μm as depicted in Fig. 3.11.

3.3.5 Resistivity measurement

The electrical transport properties of the samples were studied in the form of change in resistivity with respect to temperature using a standard four probe technique. The Fig. 3.12 shows the plot of resistivity versus temperature of samples M2 and M3.

![Graph showing variation of resistivity with temperature for samples M2 and M3.](image)

**Fig. 3.12:** Variation of resistivity with decrease in temperature for sample M2 and M3. Inset shows variation of normalized resistivity for sample M1
The inset in Fig. 3.12 shows the plot of normalized resistance versus temperature. This plot gives more clear representation of relative increase in resistance for sample M1. It can be seen that for sample M1, the resistance increases with decrease in temperature, attains a maximum value at 28K and then decreases. This indicates that the sample M1 has mixed phases. The increase in resistance corresponds to the semiconducting nature which may be due to presence of unreacted phase of boron in the sample. The low temperature region (below 28K) corresponds to the region in which the mobility of the charge carriers increases owing to enhancement in their drift velocities causing the sudden decrease in resistance. This can be possible with the presence of traces of MgB$_2$ which provides sufficient percolative paths amongst the semiconducting or insulating regions and results in decrease in resistance but incomplete transition. This is in concurrence with the XRD result for the sample M1 wherein traces of MgB$_2$ are noticed. Unlike sample M1, samples M2 and M3 show a decrease in resistivity with decrease in temperature before it ultimately shows superconducting transition. As depicted from figure, sample M2 has a higher $\rho(300K)$ value of 184.9 µΩ cm as compared to 124.0 µΩ cm value for sample M3. Though $\rho(300K)$ value for sample M2 is higher than that for M3 both the samples have nearly same $\rho(40K)$ value (79.7 µΩ cm and 77.0 µΩ cm for M2 and M3 respectively). This means that in case of sample M2 the rate of decrease in resistivity with temperature is more than that in sample M3. But, the overall resistivity of sample M3 is less than that of sample M2. This means that though the mean free path in case of both the sample is more or less same around 40 K, it gradually increases with temperature for sample M2 as compared to sample M3 [25]. This signifies the presence of greater scattering centers in sample M2 as a consequence of incomplete and discontinuous growth of MgB$_2$ phase due to insufficient nucleation centers during the synthesis of sample. This is
in line with the discontinuous island like morphology observed in SEM micrograph of sample M2. As the amount of Mg is increased in sample M3, the overall resistance gets reduced indicating better overall connectivity in the sample. This is further reflected through the relatively sharper superconducting transition with the transition width of $\Delta T_c=1.1K$. The comparatively better and continuous growth is confirmed from the cannibalistic grain growth morphology as seen in the SEM micrograph for sample M3. This is in support with the enhanced peaks of MgB$_2$ as seen in the XRD of sample M3. Moreover, sample M2 shows a broad superconducting transition extending over a temperature range of 5K with onset at 23K. This again indicates poor grain connectivity in the sample. In contrast, M3 sample shows comparatively sharp transition at 33.5K with 1.1K transition width and hence considered as an optimized sample. The $T_c$ observed in sample M3 is smaller than the standard value ($T_c=39K$) for pristine MgB$_2$ [2, 26, 27] samples and is in good agreement with the $T_c$ for the sample of the said carbon content as reported earlier [6, 8, 28-31]. This lower value of $T_c$ is attributed mainly to increase in electron scattering due to doping of carbon in the sample [5, 6, 32-34]. The residual resistivity ratio (RRR) $R(300K)/R(40K)$, was calculated to be 1.7 which is again smaller than that of pristine MgB$_2$ [32, 33, 35]. In general the observed lower values of RRR are due to presence of defects. The major possible defect in the present case is due to carbon doping in to the sample.

### 3.3.6 Magnetic susceptibility measurement

The zero field cooled (ZFC) and field cooled (FC) measurements were carried out to reaffirm the superconductivity and reproducibility observed in the optimized M3 sample and to study its magnetization behavior with temperature. Fig. 3.13 shows a sharp and one step superconducting drop at
about 33.5 K in ZFC part of magnetization, which is in agreement with value depicted from the resistivity measurement.

![Graph](image)

**Fig. 3.13:** ZFC and FC plot at 10 Oe for the sample M3 with respect to temperature.

The value of $T_c$ is well beyond 23K, the limit assigned by Liu et al. for dirty superconductor. This indicates that the samples are still under clean limit [36]. The plot drops at about 33.5 K and attains more or less constant value at lower temperatures without any remarkable rounding. Thus the ZFC plot shows nearly complete expulsion of magnetic flux lines from the sample in the superconducting state and shows perfect diamagnetism which is a clear signature of Meissner effect in the sample. This ZFC response from the sample justifies the credibility of the sample. In case of field cooled measurement,
sample was cooled under the applied magnetic field of 10 Oe and the plot of magnetization versus temperature was recorded. It showed a remarkable suppression of diamagnetic signal observed in case of ZFC measurements. Instead, it showed a slight paramagnetic signal when cooled under field. This indicates that there is a magnetic flux trapped inside the sample which inherit the perfect diamagnetism. This is what is known as Wohlleben effect or paramagnetic Meissner effect (PME) [37, 38]. The FC plot showed a transition at the temperature same as that in case of zero field cooled case, thus again confirming the superconductivity in the sample. It is well known that for the highly pinned samples, FC transition is quite weak as is observed in case of our sample [39]. The observation of PME indicates a strong pinning in the samples which is known to be due to formation of SNS/SIS type of structures at micron level [40, 41]. This is in fact, in good agreement with XRD study for the sample M3 in which the occurrence of small amount of phases other than MgB$_2$ are observed which may take part in formation of SNS or SIS structure. This may act as an essential factor in enhancement of critical current density of the sample and could prevent flux jumps.

3.3.7 $M(H)$ response of the sample

The $M(H)$ plot for the sample M3 at three different temperatures 2.5, 10 and 20 K in the applied field range of -$7 \ T \leq H \leq 7 \ T$ is shown in Fig. 3.14. It can be noticed that the magnetic moment initially drops rapidly up to about 900, 600 and 300 emu/cm$^2$ at 2.5, 10 and 20 K respectively in the lower field region and exhibits a rather open loop at higher fields. The figure shows a complete symmetric nature of $M(H)$ loop without any signature of vortex instability resulting from vortex avalanche in the low field regions. This is true for the measurements carried out at a low temperature of 2.5 K as well as for relatively higher temperatures of 20 K unlike the discrepancy observed
at low and high temperatures [42]. This indicates that the sample is free from the vortex avalanche and has a better flux pinning properties. This leads to comparatively enhanced and proper estimation of $J_c$ values. The $H_{irr}$ values can be estimated from the plots and were found to be to be 5 and 7 T respectively at 20 and 10 K except for the plot at 2.5 K, where it still remains open as seen in the inset, indicating that it might approach $H_{irr}$ values up to 8 T.

**Fig. 3.14:** Magnetic hysteresis $M(H)$ plots for the sample M3 at 2.5, 10 and 20K. Inset shows enlarged $M(H)$ plot for sample M3 at 2.5 K.
3.3.8 Critical current density measurement

The $J_c(H,T)$ plots as shown in Fig. 3.15 are extracted from M(H) loops by invoking Beans critical state [43] model using the formula (3.2),

$$J_c = 30 \times \left( \frac{\Delta M}{d} \right) \left( \frac{10}{4\pi} \right) (A/cm^2)$$

.........................(3.2)

where $\Delta M$ is the width of the magnetization curve derived from the behavior of magnetization against field and $d$ is the diameter of the sample. Here $d$ is considered as the diameter of the sample used which was maintained nearly in a cylindrical shape.

Fig. 3.15: Magnetic critical current density plots for the sample M3 at 2.5, 10 and 20 K.
The $J_c$ values at zero fields are $5.6 \times 10^5$, $4.4 \times 10^5$ and $2.5 \times 10^5$ A/cm$^2$ at 2.5, 10 and 20 K respectively. The $J_c(H)$ plots though drops rapidly at lower fields, engulfs a sufficiently larger area under it at higher fields. This indicates a relatively competitive $J_c$ values at higher fields (>3T). It is interesting to note a high $J_c$ values in our sample which may be due to doping of carbon [44] in to the MgB$_2$ lattice at boron sites as well as at interstitials. These act as effective pinning centers [45] along with some amount of MgO and enhance the flux pinning in the sample. This is in agreement with the flux jump free M(H) as well as magnetization plots. The irreversibility field values were estimated for the sample from the $J_c(H)$ using the 100 A/cm$^2$ criterion which came out to be 7, 5.6 and 3.1 T at 2.5, 10 and 20 K respectively.

3.3.9 Flux pinning plots

The normalized flux pinning force density ($F_p$) behavior of the samples as a function of increasing field at temperatures T=2.5, 10 and 20 K is shown in Fig. 3.16. The flux pinning force at a particular temperature was calculated from the critical current density and applied field by the relation (3.3) that can be described as [46-48],

$$F_p = \mu_0 J_c(H) H \quad \text{..........................(3.3)}$$

where $\mu_0$ is the magnetic permeability in vacuum. It can be observed that the flux pinning values for the samples first increases, then reaches at a peak value and then decreases up to the irreversibility field value. Thus, the flux pinning curves shows a linear behavior in the low field region up to a peak where the flux pinning force is maximum. The pinning force values then decrease following a quadratic behavior as the applied field increases. This behavior exhibited by the sample is typical for MgB$_2$ [47]. It is interesting to
note that with increase in temperature though the broadness of the curve decreases, the peak position remains more or less same. This suggests that the maximum in the flux pinning force is independent of the temperature up to at least 20K, and the sample has strong pinning stability without any observation of flux jumps.

![Flux pinning plots for the sample M3 at the temperatures 2.5, 10 and 20 K.](image)

**Fig. 3.16:** Flux pinning plots for the sample M3 at the temperatures 2.5, 10 and 20 K.

As far as the type of pinning is concerned, it can be considered as the combination of grain boundary pinning which is prominent in case of MgB$_2$, pinning due to presence of carbon as well as insulating impurities such as
MgO which may be present outside the lattice and the pinning due to point defects which arise from carbon inclusion in MgB$_2$ matrix [48].

3.4 Conclusions

In conclusion, the successful synthesis of carbon doped MgB$_2$ samples under carbon induced virtual inert atmosphere is achieved where carbon was used as a buffer to assist the reaction between Mg and B to form MgB$_2$. It was found that the sample with lower Mg content resulted in magnesium deficient phases of MgB$_4$ and presence of unreacted B instead of MgB$_2$. This in turn gives a semiconducting nature to the sample as shown by negative temperature dependence of resistivity. As the amount of Mg increases, the unreacted B as well as Mg deficient phase disappears completely and the growth of MgB$_2$ phase is observed. The optimized sample with B:Mg ratio of 1:1.5 exhibited sharp superconducting transition at about 33.5K with features of paramagnetic Meissner effect indicating strong pinning effects in this superconducting sample. The occurrence of lower T$_c$ value can be attributed to carbon substitution at B sites in MgB$_2$ structure. The carbon doping results in contraction of in-plane lattice parameter ‘a’ from 3.086 to 3.061 Å. The amount of carbon doped in the sample was estimated and represented as MgB$_{1.8}$C$_{0.2}$. This doping of carbon in the sample resulted in the enhancement of critical current density of the sample which turned out to be 5.6×10$^5$, 4.4×10$^5$ and 2.5×10$^5$ A/cm$^2$ at 2.5, 10 and 20 K respectively under self fields. The flux pinning plots shows that the magnetic flux are well pinned by the flux pinning centers in the synthesized carbon doped MgB$_2$ superconducting sample without any signature of flux jump.
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References

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