4.1: Introduction

MgB$_2$ is certainly a beneficial superconductor due to its strong grain coupling for superconducting current, long coherence length, high carrier density, low electromagnetic anisotropy, and simple binary composition without expensive elements. It has already been fabricated in the form of bulk, single crystals, thin films, tapes and wires. Moreover, the $J_C$ of pristine MgB$_2$ bulk at low magnetic fields is high enough for low field applications. But it rapidly decreases with an increase of magnetic field due to low $H_{C2}$ and lack of effective pinning sites. Therefore, both the enhancement of $H_{C2}$ and the introduction of effective pinning sites are essential to improve $J_C$ under high magnetic fields for its practical application [1, 2]. Significant research has been done in developing various techniques like irradiation of energetic ions or neutron and chemical doping for the improvement of flux pinning and hence $J_C(H)$ and $H_{C2}$ in MgB$_2$ [3-8]. Among these, chemical doping is an effective and easy method for modifying the properties of MgB$_2$. Doping of elements or compounds into MgB$_2$ accompanies element substitution and/or inclusion of impurity particles. In the former case, changes of electronic state, lattice constants and crystallinity are expected to occur; while in the latter case, impurity particles are expected to be dispersed as inclusions throughout the MgB$_2$ matrix so as to act as effective pinning sites. Elemental substitution at Mg/B site introduces defects in the MgB$_2$ structure which decreases the mean free path of the normal electrons and creates local pinning centers. This consequently increases the $H_{C2}$ and irreversibility line. Another expected effect of doping is the suppression of the grain growth of MgB$_2$. Of the various dopants tried for substitution in MgB$_2$, carbon containing compounds seem to be the most effective. On considering doping via inclusion of impurities, the particle size of the additive used is very important. The addition of nano sized dopants is found...
Effect of processing temperature and nano dopants on bulk MgB$_2$

to be much effective in MgB$_2$, since it leads to the formation of nano particle secondary phase inclusions comparable to the coherence length of MgB$_2$ and thereby enhances the grain connectivity and flux pinning.

4.2: Preparation and characterization of bulk MgB$_2$

Bulk MgB$_2$ samples were prepared by *in situ* Powder In Sealed Tube (PIST) method [9-10]. Stainless steel (SS) SUS 304 tubes of 10 cm length with an OD of 10 mm and ID of 8 mm were used for synthesis. One end of the tube was pressed uniaxially (~ 1 GPa) using a hydraulic press so that it became bar shaped. Stoichiometric weights of Mg powder (-325 #, <50 µm, 99.8 %) and B powder (-325 #, <50 µm, 99 %, amorphous) were taken using an electronic balance. Powders were mixed and ground thoroughly in air for about 30 minutes to get homogeneous fine powder using an agate mortar and pestle. Then the powder mixture was densely packed through the open end of the pressed SS tube leaving some space unfilled. The unfilled portion was pressed with the same pressure as that of previous end such that both the pressed ends are of equal length. Subsequently, the powder filled middle area was again subjected to uniaxial pressing to get a bar shaped portion. End sealing was performed by arc welding in order to avoid the escape of volatile Mg. A wet cloth was wound around the specimen during welding to avoid heating up of the sample. Samples were then heat treated directly in air at desired temperatures in a programmable muffle furnace with a ramp rate of 5 °C/min and subsequently performed furnace cooling. Then, bar shaped MgB$_2$ core was taken out by mechanically peeling off the SS sheath for XRD, SEM and magnetic measurements.

The structural and phase analysis of the samples were performed using an X-ray diffractometer. Phase identification of the samples was performed using X’Pert Highscore Software in support with ICDD PDF II database. The grain morphology and microstructure were examined by SEM and HRTEM. DC magnetic measurements were carried out using a SQUID/VSM based magnetometer on cut pieces having dimensions of 3×3×1.5 mm, with applied field along the longest dimension. The
preparation and characterization of bulk MgB₂ samples has been given in chapter 3 and the same is pursued in the following sections.

4.3: Pristine MgB₂: Effect of processing temperature on structural and superconducting properties

4.3.1: Introduction

Considerable efforts have been made on the synthesis of samples in the form of bulk, thin film, tape and wire. The factors such as purity and size distribution of precursor powder, fabrication procedures and heat treatment schedule influence the superconducting properties of bulk MgB₂. There are two main routes to prepare bulk MgB₂: one, based on the reaction of pure elements (in situ technique) [11-13] and the other, sintering of pre-reacted MgB₂ powders (ex situ technique) [14-16]. Of which in situ method is more preferred since it provides better grain connectivity and effective control of pinning centers. Improvement in \( J_c(H) \), \( H_{c2} \) and \( H_{irr} \) is the key factor for practical applications of MgB₂ superconductor and this depends sensitively on flux pinning, grain connectivity, density, chemical composition and microstructure. MgO phase at the grain boundaries is the major impurity in the in situ synthesized MgB₂ that severely affects the \( J_c \). The MgO at the grain boundaries acts as weak links and significantly reduces the intergrain \( J_c \) [17].

Several synthesis procedures have been reported for in situ bulk MgB₂ synthesis. Generally, the synthesis is done by enclosing samples in Nb/Ta tubes or foils in inert atmosphere or vacuum. The maximum \( J_c \) reported is only in the range \( 10^2-10^4 \, \text{A/cm}^2 \) at 20 K and 2 T [18-21]. This is due to high volatility of Mg at elevated temperatures resulting in high porosity and poor superconducting properties. Although reasonably dense bulk MgB₂ samples were obtained under hot pressing of specimen at high pressure and high temperature, the large scale exploitation of MgB₂ as a potential material for various practical applications requires the development of more simple and cost effective processing techniques [22-25]. The method we used for bulk MgB₂ synthesis is in situ PIST technique in which the ends of the powder filled tubes were pressed and sealed by ‘cold-welding’ so that the samples can be heat treated directly in air. This
can practically eliminate Mg evaporation loss and minimize oxidation of Mg and reduce the cost of synthesis by avoiding expensive Nb/Ta tubes or foils, inert gases and special furnaces. For *in situ* synthesis of MgB$_2$, the synthesis method and processing temperature have strong influence on the phase formation, crystallinity and microstructure and hence on the superconducting properties of the material. Therefore, an attempt has been made to optimize the processing temperature of bulk MgB$_2$ using PIST method. The melting point of Mg, a precursor for MgB$_2$, is around 650 °C. But MgB$_2$ processed at temperatures even up to 750 °C showed the presence of unreacted Mg. Moreover, at temperatures above 900 °C, the formation of MgO was found to increase. Hence, to tune the optimum processing temperature which yields the best properties for MgB$_2$, a temperature range 750-900 °C was chosen. The samples were heat treated at 750, 800, 850, and 900 °C for 2 hrs and named as MB750, MB800, MB850 and MB900 respectively.

### 4.3.2: Results and discussion

*Figure 4.1* shows powder XRD patterns of bulk MgB$_2$ heat treated at different temperatures 750, 800, 850, and 900 °C for 2 hrs. All the XRD patterns show sharp peaks of MgB$_2$ phase with only a minute fraction of MgO. Traces of MgO observed are due to the entrapped air in the reaction mixture before end sealing of the tubes. Small amount of unreacted residual Mg is detected for the sample heat treated at 750 °C. This is because the melting point of Mg is around 650 °C, which is very much less than that of B (2080 °C) and so the kinetics of the expected liquid-solid reaction between Mg and B is not fast enough at this temperature to complete the reaction. However, MgB$_2$ peaks become sharper and stronger as the heat treatment temperature increases which indicate increase in phase purity and/or crystallinity. Absence of the peaks corresponding to MgB$_4$ or other higher borides in all the samples confirms that there is no evaporation of Mg during the heat treatment process. Moreover, absence of the peaks corresponding to Fe and Fe containing compounds indicates that there is no interfacial reaction occurring between Mg/B/MgB$_2$ and SS sheath at these temperatures.
Effect of processing temperature and nano dopants on bulk MgB$_2$

Figure 4.1: XRD patterns of MgB$_2$ samples heat treated at different temperatures (750, 800, 850 and 900 °C)

Figure 4.2: Variation of (a) Lattice parameters $a$ & $c$ and (b) FWHM of (100), (101), (002) and (110) peaks of MgB$_2$ samples with processing temperature

Lattice parameters $a$, $c$ and full width at half maximum (FWHM) of the (100), (101), (002) and (110) peaks of the samples are shown in figure 4.2. The lattice parameters are calculated from XRD for hexagonal structure with space group $p6/mmm$. The samples show no significant variations in lattice parameters within the experimental error. FWHM of all the peaks decreases significantly on increasing the sintering temperature indicating the increase in grain size of MgB$_2$ with temperature.
To analyze the effect of grain size on peak broadening and study the morphological features, microstructural examination of the samples is carried out using SEM. Figure 4.3 shows typical SEM images of the fractured MgB$_2$ samples heat treated at 750, 800, 850, and 900 °C. The microstructure of the samples is homogenous in nature. The samples show fine hexagonal and randomly oriented MgB$_2$ grains. SEM images also show that the average grain size of the crystalline MgB$_2$ increases with sintering temperature, well in agreement with the decrease of FWHM from XRD. It is to be noted that the smaller grain size of pure MgB$_2$ processed at lower temperatures increases the number of grains which in turn enhances the density of grain boundaries. In pure MgB$_2$, grain boundaries are the main flux pinners [26, 27]. Hence, the increased number of grains contributes to enhance the flux pinning property and hence the $J_C(H)$ characteristics of the samples processed at relatively low temperatures.

Temperature dependence of magnetization ($M$-$T$) of the samples is shown in figure 4.4. All the samples show sharp superconducting transitions with $T_C$ around 38.5 K and $\Delta T_C$ ($T_{c90\%}$ - $T_{c10\%}$) $\sim$ 1 K indicating the high
phase purity and homogeneity of MgB$_2$ samples sintered at different temperatures. Almost identical $T_C$ and $\Delta T_C$ values of the samples indicate that the final stoichiometry of all the samples are same and samples are identical with respect to lattice or structural defects and electronic states in the superconducting B planes.

Figure 4.4: DC magnetic susceptibility versus temperature plots of MgB$_2$ samples processed at different temperatures

Figure 4.5: $J_C(H)$ curves of MgB$_2$ samples synthesized at different temperatures. Closed and open symbols represent $J_C(H)$ at 10 K and 20 K respectively
The critical current density $J_C$ of the bulk MgB$_2$ samples was calculated from the width of the magnetization hysteresis ($M$-$H$) loops on the basis of the Bean critical state model [28]. Figure 4.5 illustrates the dependence of $J_C$ on applied magnetic fields up to 5 T of MgB$_2$ samples at 10 K and 20 K. At 10 K, $J_C$ jumps abruptly at low fields where the estimation of $J_C$ may not be accurate due to the flux jumps whereas $J_C(H)$ follows a systematic behavior in higher fields for all the samples. Sample heat treated at 800 °C shows the highest $J_C$ in external fields at both 10 K and 20 K. It is found that the $J_C(H)$ performance is better for the samples heat treated at lower sintering temperatures (750 °C and 800 °C), while it is lower for the samples heat treated at higher sintering temperatures (850 °C and 900 °C).

Figure 4.6: $F_P(H)$ curves of the MgB$_2$ samples heat treated at different temperatures

Figure 4.6 shows the field dependence of flux pinning force density, $F_P$ ($F_P = J_C \times H$) of MgB$_2$ samples heat treated at different temperatures which was calculated from the $J_C(H)$ data measured at 10 K. Since the flux jumps show significant marks on the shape of the $F_P(H)$ curves, the curves are plotted after refining the $J_C(H)$ data up to 2 T. The samples heat treated at relatively lower temperatures (MB750 and MB800) showed enhanced flux pinning as compared to those processed at higher temperatures. The reduced grain size and hence the increased grain
boundary is the main reason behind the improved flux pinning and $J_c(H)$ for the samples sintered at lower temperatures.

**4.3.3: Conclusion**

The superconducting properties of bulk *in situ* PIST MgB$_2$ at different temperatures were studied. XRD analysis gives sharp peaks of MgB$_2$ phase with only a minute fraction of MgO. Well crystallized MgB$_2$ grains are formed in all the samples processed at temperatures in the range 750-900 °C and the grain size is found to increase with temperature. All the samples show sharp diamagnetic transitions at 38.5 K, independent of the processing temperature of samples whereas the in-field $J_c$ shows distinctly different behavior for the samples heat treated at different temperatures. Both FWHM and SEM confirm the reduction in grain size which in turn increases the density of grain boundaries. This is the main reason behind the improved flux pinning and hence $J_c(H)$ for the samples sintered at lower temperatures. Therefore, it can be concluded that 800 °C is the optimum processing temperature for bulk MgB$_2$ since it gives the best $J_c(H)$ performance when compared to the rest.

**4.4: Nano oxide doped MgB$_2$: A comparative study on structural and superconducting properties**

**4.4.1: Introduction**

Doping with rare earth (RE) elements has little effects on $T_C$ of MgB$_2$ due to the low solid solubility of RE elements in the MgB$_2$ lattice as well as the relatively localized 4f electrons. The paramagnetism of the rare earth metals originates from their inner 4f electrons which are rather localized [29]. The itinerant 3d electrons of transition metals may interact with the conduction electrons of the system whereas the localized 4f electrons do not interact with the conduction electrons, thus superconductivity is not suppressed by the RE elements while it is remarkably suppressed by ferromagnetic elements. Hence, rare earth oxide dopants are good candidates to enhance flux pinning properties of MgB$_2$. It has been reported that doped rare earth oxides (REO) give rise to REB$_6$ and REB$_4$ impurity precipitates which get embedded into the MgB$_2$ matrix and
work as effective pinning centers; significantly improving $J_C$ and $H_{irr}$ of MgB$_2$ [30-35]. Here, typical nano sized rare earth oxides like nano Tb$_4$O$_7$ (n-Tb$_4$O$_7$), nano Ho$_2$O$_3$ (n-Ho$_2$O$_3$) and a non rare earth oxide, nano SiO$_2$ (n-SiO$_2$), have been chosen for studying their effect on bulk MgB$_2$. The weight percentage of dopant to be added was fixed after analyzing bulk MgB$_2$ samples doped with different doping levels of each nano oxides. It was seen that MgB$_2$ samples doped with 5 wt% of nano oxides gave the best $J_C(H)$ performance and hence, doped samples with 5 wt% of each nano oxide are chosen for a comparative study of their effects on MgB$_2$. Polycrystalline MgB$_2$ (MB), MgB$_2$+5 wt% n-Tb$_4$O$_7$ (MBTb), MgB$_2$+5 wt% n-Ho$_2$O$_3$ (MBHo) and MgB$_2$+5 wt% n-SiO$_2$ (MBSi) were prepared by in situ PIST method, using Mg, amorphous B, Tb$_4$O$_7$ (< 60 nm, 95+ %), Ho$_2$O$_3$ (< 60 nm, 99.5+ %) and SiO$_2$ (10 nm, 99.5 %) as starting powders. The preparation and characterization of samples are detailed in previous sections.

4.4.2: Results and discussion

![XRD patterns of pure and nano oxide doped MgB$_2$ samples](image)

Figure 4.7: XRD patterns of pure and nano oxide doped MgB$_2$ samples
Figure 4.7 shows the XRD patterns of MgB2 with different nano oxide dopants, heat treated at 800 °C for 2 hrs. MgB2 is the main phase, with a trace amount of MgO, observed in all the samples. The peak intensities of MgB2 are reduced in doped samples, indicating that the undoped sample has better phase purity and crystallinity. In n-REO doped samples, the presence of REB4 indicates that the added n-REO decomposed and reacted with B, whereas in n-SiO2 doped samples the dopant reacted with Mg to form Mg2Si. The slight MgO observed in pure sample is due to the entrapped air before end sealing of the tubes, and the amount of MgO in the doped samples is slightly higher compared to the undoped sample, which is due to the excess oxygen available from the added oxides. The a and c lattice parameters, calculated from the XRD data, for a hexagonal crystal structure, are given in table 4.1. However, the very small change in the lattice parameters may be due to the strain induced by the nano particles, rather than a substitutional effect or structural change, as suggested by Wang et al. for Y2O3 addition [30].

<table>
<thead>
<tr>
<th>Samples</th>
<th>Lattice parameters (nm)</th>
<th>$T_c$ (K)</th>
<th>$\Delta T_c$ (K)</th>
<th>$J_c$ (A/cm²) at 5 K</th>
<th>$H_{irr}$ (T) at 5 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>c</td>
<td></td>
<td>4 T ($\times 10^4$)</td>
<td>8 T ($\times 10^2$)</td>
</tr>
<tr>
<td>MB</td>
<td>0.3087</td>
<td>0.3519</td>
<td>38.6</td>
<td>1.4</td>
<td>1.8</td>
</tr>
<tr>
<td>MBTb</td>
<td>0.3087</td>
<td>0.3515</td>
<td>38.5</td>
<td>2.3</td>
<td>0.7</td>
</tr>
<tr>
<td>MBHo</td>
<td>0.3085</td>
<td>0.3517</td>
<td>38.1</td>
<td>3.5</td>
<td>1.9</td>
</tr>
<tr>
<td>MBSi</td>
<td>0.3084</td>
<td>0.3520</td>
<td>38.3</td>
<td>3.2</td>
<td>8.3</td>
</tr>
</tbody>
</table>

Figure 4.8 shows the SEM images of the fractured surfaces of pure and nano oxide doped MgB2 samples. All the samples show homogenous microstructure with tiny hexagonal and randomly oriented grains of average size around 1 µm wherein the grain boundaries are sharp and clear except for MBHo. The MBHo has tightly packed well connected MgB2 grains with size relatively smaller than the others.
Effect of processing temperature and nano dopants on bulk MgB₂

Figure 4.8: SEM images of pure and nano oxide doped MgB₂ samples

Figure 4.9: DC magnetic susceptibility vs temperature plots of pure and nano oxide doped MgB₂ samples

$M$-$T$ plots of the samples are shown in figure 4.9. All the samples show sharp superconducting transitions with $T_c$ in the range 38.1-38.6 K
and $\Delta T_c \sim 1$ K. The almost identical $T_c$ and lower $\Delta T_c$ indicate that the samples have high crystallinity and homogeneity and are not affected by any grain boundary connectivity problem. This infers that the doped nano oxides and the addition induced reacted secondary phases are incorporated within the MgB$_2$ grains rather than precipitated or segregated at the grain boundaries.

Figure 4.10: $J_c(H)$ curves of pure and nano oxide doped MgB$_2$ samples

*Figure 4.10* shows the field dependence of magnetic $J_c$ of the samples up to a field of 8 T at 5 K, deduced from $M$-$H$ data. Materials with high critical current density, high magnetic diffusivity and low heat capacity usually cause thermomagnetic flux jumps in magnetization hysteresis loop. Such thermomagnetic flux jumps are observed around 1 T for all the samples. When compared to the undoped sample, the $J_c(H)$ is enhanced for all the doped samples, for the entire field of study. At lower fields, the improvement in $J_c(H)$ is higher for n-REO doped samples but at higher fields the n-SiO$_2$ doped sample shows better $J_c(H)$ performance. The better low field $J_c$ of these n-REO doped samples indicates that the grain connectivity is not disturbed by the secondary phases precipitated by them. The enhanced $J_c(H)$ performance of MBHo at lower fields can be attributed to the improved grain connectivity as observed in SEM. As shown in *table*
it can be seen that the $J_c(H)$ and $H_{irr}$ are significantly improved for all nano oxide doped MgB$_2$ samples. The improvement in $J_c(H)$ and $H_{irr}$ of the doped samples can be due to the flux pinning caused by the nano sized secondary phases with size comparable to the coherence length of MgB$_2$.

Figure 4.11: $F_p(H)$ curves of the pure and nano oxide doped MgB$_2$ samples

In order to analyze the flux pinning behavior, $F_p$ of undoped and doped samples at 5 K is calculated (figure 4.11). Since the flux jumps show significant marks on the shape of the curves, the curves are plotted after refining the $J_c(H)$ data up to 2 T. The introduction of nano dopants in MgB$_2$, generally, increases the density and strength of flux pinning centers either by substitution or homogeneous nano inclusions (reacted or unreacted impurities). All the nano oxide doped MgB$_2$ samples show enhanced flux pinning strength up to 8 T, when compared to the pure one. The maximum flux pinning force density ($F_{p_{max}}$) values for MB, MBTb, MBHo and MBSi are 2.0, 3.5, 4.7 and 2.5 GN/m$^3$ respectively. Among all, n-Ho$_2$O$_3$ doped MgB$_2$ sample shows the maximum flux pinning behavior in the entire field of study. Ho$_2$O$_3$ causes the formation of HoB$_4$ as the reacted impurity phase, which possesses a strong magnetic moment. Since magnetic impurities like HoB$_4$ can interact more strongly with the flux lines and exert a strong force to trap the flux lines, n-Ho$_2$O$_3$ doped sample exhibits better flux pinning behavior and hence $J_c(H)$ performance.
4.4.3: Conclusion

The effect of nano oxide dopants on the microstructural and superconducting properties of in situ bulk MgB$_2$ was studied. Absence of appreciable change in lattice parameters and $T_C$, points out that the additives are not substituted at either Mg or B sites in MgB$_2$. In n-REO doped samples, the added n-REO decomposes and reacts with B to form REB$_4$ whereas in n-SiO$_2$ doped samples the dopant reacts with Mg to form Mg$_2$Si. On comparing with pure sample, the $J_c(H)$ performance is significantly enhanced for all the doped samples. The addition induced reacted phases act as strong flux pinners thereby improving the $J_c(H)$ and $H_{irr}$ of the nano oxide doped samples. Flux pinning analysis also confirms the same. The n-Ho$_2$O$_3$ doped MgB$_2$ sample shows the maximum flux pinning behavior in the entire field of study due to the presence of magnetic impurities like HoB$_4$ as strong flux pinners.

4.5: Carbon variants doped MgB$_2$: A comparative study on structural and superconducting properties

4.5.1: Introduction

Of the various elements and compounds being doped in MgB$_2$, carbon containing compounds such as SiC, C, B$_4$C and hydrocarbons have been found to be the most efficient for significant $J_c$ enhancement in high magnetic fields [36, 37]. Since MgB$_2$ is a two gap superconductor, the substitution of carbon for boron has a great impact on the carrier density and impurity scattering [38]. The $J_c(H)$ characteristics depend not only on C substitution but also on the effectiveness of the dopant in the formation and distribution of nano scale secondary phases into the grains as flux pinners. It was observed that the amount of C getting substituted and the efficacy of the resulting secondary precipitates, mostly depend on the nano additive used. In order to improve the superconducting properties especially the in-field $J_c$, an attempt has been made to study bulk MgB$_2$ samples doped with typical variants of carbon. The weight percentage of carbon dopant to be added was fixed after analyzing bulk MgB$_2$ samples doped with different doping levels of carbon (MgB$_{2+x}$C$_x$ where x: 0→0.2). It was seen that MgB$_2$ samples doped with 2.6 wt% of carbon dopant (MgB$_{1.9}$C$_{0.1}$) gave the best
$J_c(H)$ performance [39]. Hence, all the doped variants of MgB$_2$ containing 2.6 wt% of carbon are chosen for a comparative study of their effects on structural and superconducting properties of MgB$_2$. The carbon variants such as nano diamond (n-D), nano carbon (n-C), nano silicon carbide (n-SiC) and burned rice husk (BRH) are used in the present study.

Considering the significant improvement in $J_c(H)$ by n-SiC and n-C additions [39, 40], BRH is explored as an alternative low cost replacement of these expensive nano dopants. BRH is a nonconventional raw material of SiC which contains ultra fine amorphous silica (SiO$_2$) and carbon. The presence of amorphous SiO$_2$ in a matrix of friable carbon, easy availability and low cost make BRH a promising dopant for MgB$_2$. The ratio of SiO$_2$ to C in BRH can be optimized by controlling the burning temperature of rice husk. The structural and superconducting properties of all the nano sized carbon variants mentioned above are compared with the best result obtained for BRH doped MgB$_2$ (5 wt%).

Polycrystalline bulk MgB$_2$ and its doped variants (dopants: n-D, n-C, n-SiC and BRH) were prepared by in situ PIST method using Mg, amorphous B, n-D (< 10 nm, 95+ %), n-C (< 50 nm, 99+ %), n-SiC (< 100 nm, 97.5+ %) and BRH as the starting materials. The BRH used here was prepared by heating the raw rice husk at 300 °C for 1 hr. Figure 4.12(a) shows the powder XRD pattern of the BRH powder which gives only a broadened peak of SiO$_2$, indicating its amorphous nature. Since the XRD doesn’t show the presence of amorphous C, EDX analysis of BRH was also carried out which confirmed the presence of Si (~40 wt%), O (~10 wt%)
and C (~50 wt%) as shown in figure 4.12(b). The preparation and characterization of samples are detailed in previous sections. The MgB$_2$ samples, pure and those doped with n-D, n-C, n-SiC and BRH, are named as MB, MBD, MBC, MBS and MBR respectively.

### 4.5.2: Results and discussion

**Figure 4.13** shows the XRD patterns of pure and carbon variants doped MgB$_2$ samples. All the samples show MgB$_2$ as the main phase with a trace amount of MgO. The MgO formation is due to entrapped air before the end sealing of the tubes. For n-D doped sample, slight amount of unreacted Mg is detected apart from MgO even at low level doping. The presence of unreacted Mg and the absence of any C containing secondary phases in MBD indicate the relatively low reactivity of n-D at the synthesis temperature of 800 °C. But for MBC, no impurity phases (including C containing secondary phases) other than MgO are detected. The MBS shows Mg$_2$Si and traces of unreacted SiC as impurity phases and the presence of Mg$_2$Si confirms the dissociation of SiC which is consistent with earlier works [41]. While the dissociated Si reacts with Mg to form Mg$_2$Si, the remaining free C is incorporated into the MgB$_2$ lattice. The XRD pattern of
MBR shows Mg$_2$Si and MgO as main impurity phases wherein the MgO content is much higher compared to the other doped samples. Hence, it is clear that SiO$_2$ contained in BRH reacts with Mg to form Mg$_2$Si and MgO and the remaining C substitutes at B site.

For all doped samples, the (110) peak of MgB$_2$ which is related to the in-plane lattice constant shifts to higher angles, which shows a decrease in lattice parameter $a$ indicating that substitution of C atom into the B site has occurred. On the other hand, the (002) peaks undergo a relatively small shift. This means that the lattice parameter $c$ does not vary significantly within the range of dopants studied but the lattice parameter $a$ decreases when these dopants are added. The lattice parameter $a$ of the hexagonal structure of MgB$_2$ are calculated and tabulated in table 4.2. As can be seen, among all the doped samples the lattice parameter $a$ is decreased to a maximum extent for the MBC whereas it is the least for MBD. However, in the case of MBS and MBR, the value of $a$ is comparable to that of MBC. This implies that the level of substitute d C is highest in the case of MBC, MBS and MBR samples while it is lesser for MBD at identical processing conditions. The decrease of $a$ axis is an indication of the C substitution for B, which is further proven by the depression of the $T_c$ of all the doped samples. It is expected that C, which has one more electron than B, will donate electrons to the $\sigma$ band. Also, an increase of impurity scattering within the $\pi$ band and the modification of band structure are achieved by C substitution [42, 43].

Table 4.2 shows the full width at half maximum (FWHM) of (100), (101), (002) and (110) peaks of carbon variants doped and undoped MgB$_2$ samples. It is seen that the values of the FWHM sharply vary from pure to doped samples except for (002) peak. Since (100) and (110) peaks reflect the in-plane lattice constant of honeycomb boron lattice, the broadening of these peaks suggests the occurrence of some distortion in the lattice due to C substitution at B site. This result is consistent with the earlier reports in which the FWHM of these peaks has a positive correlation with the $H_{irr}$ of MgB$_2$, i.e. $H_{irr}$ increases with increasing FWHM [44, 45]. Since the honeycomb boron lattice is responsible for superconductivity in MgB$_2$, the distortion results in the impurity induced scattering of charge carriers and
thus enhances critical field through a reduction of coherence length. But the out-of-plane FWHM of (002) is practically independent of carbon dopants. These results strongly indicate that the in-plane structure was selectively disordered by the C substitution at B site. It may be noted that a decrease in grain size could also result in peak broadening.

Table 4.2: Structural properties of pure and carbon variants doped MgB₂ samples

<table>
<thead>
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<th>Samples</th>
<th>Lattice parameters (nm)</th>
<th>FWHM (degree)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>c</td>
<td>(100)</td>
</tr>
<tr>
<td>MB</td>
<td>0.3087</td>
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<td>0.155</td>
</tr>
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<td>0.267</td>
</tr>
</tbody>
</table>

Figure 4.14 shows SEM images of the fractured surfaces of the undoped and carbon variants doped MgB₂ samples. The undoped sample shows a homogenous microstructure with tiny and well packed hexagonal grains of average size 1 μm where grain boundaries are sharp and clear. In MBC and MBR samples, the grains are found to be more packed with increasing density of grain boundaries whereas MBD and MBS samples show a homogenous mixture of smaller and larger grains. The smaller grain size will increase the density of grain boundaries thereby enhancing the flux pinning property and $J_c(H)$ characteristics of doped samples. Figure 4.14(f) shows HRTEM micrograph and corresponding EDX analysis of MBR. It is clear that the impurities in the BRH doped sample is homogenously distributed within the MgB₂ grains. These uniformly distributed impurities with size (~10 nm) comparable to the coherence length of MgB₂ can pin the flux lines within the grains. EDX analysis reveals that the intragrain impurities are Mg, B, C, Si and O (The excessive peak intensity in respect of C is due to the additional contribution from the carbon present in the sample grid). This finding supports the XRD result that the secondary
phases/inclusions are Mg$_2$Si and MgO. These intragrain nano sized inclusions and the crystal defects created by C substitution act as strong pinning centers and are responsible for the improved flux pinning in the BRH doped sample.

Figure 4.14: (a)-(e) SEM images of pure and carbon variants doped MgB$_2$ samples. (f) HRTEM image of MBR sample (inset shows EDX analysis of the same sample)
Temperature dependence of zero field cooled magnetization values \((M-T)\) for the undoped and doped samples are shown in figure 4.15. \(T_C\) is defined as the onset temperature at which the samples exhibit diamagnetic properties and the measured values of \(T_C\) are tabulated in table 4.3. As shown in table, the undoped sample has a \(T_C\) of 38.6 K which decreases by 1-3 K in doped samples. This is expected due to the C substitution at the B site. The substitution of C at the B site reduces the hole concentration and causes changes in the phonon modes. The reduced density of states and weakened electron-phonon coupling are the reasons for \(T_C\) reduction in the doped samples. The decrease is more in the case of MBS compared to MBC and MBD. The unreacted Mg in case of n-D and unreacted SiC and Mg$_2$Si in case of n-SiC doped samples are also responsible for \(T_C\) decrease in the doped samples. \(\Delta T_C\) of the samples is also determined and tabulated in table 4.3. The undoped sample has a \(\Delta T_C\) of 1 K, which increases to 1.3-2.1 K for the doped samples. Among the doped samples, the MBR and MBC samples show lower \(\Delta T_C\) values. The comparatively higher \(\Delta T_C\) of other doped samples indicates that both C substitution and the presence of non-superconducting phases reduce crystallinity and sample homogeneity, as seen in XRD.
Table 4.3: Superconducting properties of pure and carbon variants doped MgB$_2$
samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_C$ (K)</th>
<th>$\Delta T_C$ (K)</th>
<th>$J_C$ (A/cm$^2$) at 5 K</th>
<th>$F_{P_{max}}$ (GN/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>4 T ($\times10^4$)</td>
<td>8 T ($\times10^3$)</td>
</tr>
<tr>
<td>MB</td>
<td>38.6</td>
<td>1.0</td>
<td>1.4</td>
<td>0.1</td>
</tr>
<tr>
<td>MBD</td>
<td>36.7</td>
<td>2.0</td>
<td>1.9</td>
<td>1.4</td>
</tr>
<tr>
<td>MBC</td>
<td>36.3</td>
<td>1.3</td>
<td>4.9</td>
<td>5.1</td>
</tr>
<tr>
<td>MBS</td>
<td>35.8</td>
<td>2.1</td>
<td>3.6</td>
<td>4.9</td>
</tr>
<tr>
<td>MBR</td>
<td>37.7</td>
<td>1.0</td>
<td>5.2</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Figure 4.16: $J_C(H)$ curves of pure and carbon variants doped MgB$_2$ samples

The magnetic field dependence of $J_C$, calculated from magnetic hysteresis measurements at 5 K for all samples is illustrated in figure 4.16. $J_C$ jumps abruptly at lower fields due to the flux jump. For the undoped sample, $J_C$ drops rapidly in the presence of magnetic field but, at higher fields, all the doped samples show significant enhancement in $J_C(H)$ behavior with respect to the pure sample. For MBD, $J_C$ value is much lower when compared with the other doped samples. This implies that at lower
fields, the presence of excess Mg (as seen in XRD) reduces the \( J_C \) and at higher fields, the partial substitution of C gives moderately higher \( J_C \) as compared to pure sample. Of all the doped samples, MBC and MBR give the best \( J_C \) performance up to the maximum field studied (8 T) and the level of \( J_C \) enhancement is around 50 times greater than the undoped sample at 5 K (8 T). MBS also shows considerably improved \( J_C(H) \) behavior at higher fields, but it exhibits lower \( J_C \) values compared to MBC and MBR at lower fields. This implies that the secondary non-superconducting phases observed in these samples affect the grain connectivity and hinder the flow of super current at lower fields. The contribution towards the \( J_C \) enhancement in MBS and MBR comes partly due to C substitution and partly due to the presence of reacted phase Mg\(_2\)Si as flux pinners. But for MBC, C substitution solely is the reason for significant enhancement of \( J_C \) at higher fields.

Figure 4.17: \( F_p(H) \) curves for the pure and carbon variants doped MgB\(_2\) samples

Figure 4.17 shows the bulk \( F_p(H) \) curves of the pure and carbon variants doped MgB\(_2\) samples. Since the flux jumps show significant marks on the shape of the curves, the curves are plotted after refining the \( J_C(H) \) data up to 2 T. Here, the \( F_p \) of the sample doped with BRH is significantly enhanced for the entire field of study as compared to pure and other doped
samples and the maximum flux pinning force density \((F_{\text{pin}})\) for MBR is 3 GN/m\(^3\) (table 4.3). It is also observed that the C substitution at B site causes a shift in \(F_{\text{pin}}\) of all the doped samples towards high field, except for MBD. In MBR, both C substitution at the B site and the reaction induced secondary phase Mg\(_2\)Si contribute to further pinning and these are the main reasons for the significant enhancement in \(F_p\) and hence \(J_c(H)\) performance. The \(F_p\) of MBC also shows significant enhancement at higher fields and here C substitution is solely the reason for flux pinning. In the case of MBS, both C substitution and the presence of Mg\(_2\)Si are the reasons for the enhancement of flux pinning at higher fields. Among all the doped samples, MBD shows poor flux pinning behavior due to the low reactivity of n-D.

### 4.5.3: Conclusion

A comparative study on the effect of doping of n-D, n-C, n-SiC and BRH in MgB\(_2\) was carried out under identical doping levels of C and processing conditions. The XRD analysis shows no reacted or unreacted phases in the case of n-C doped sample, while all other doped samples show unreacted or/and reacted phases. Both \(a\) axis shrinkage and FWHM variation observed in all the carbon variant doped samples confirm the C substitution at B site. Although C substitution together with the presence of non-superconducting phases decreases the \(T_c\) to a small extent, the \(J_c(H)\) performance of all the doped samples enhances significantly. On comparing all the doped samples, n-C, n-SiC and BRH doped samples competitively exhibit highly enhanced \(J_c(H)\). In the case of n-SiC and BRH doped samples, both C substitution and the presence of Mg\(_2\)Si causes enhanced flux pinning and hence \(J_c(H)\), while for n-C doped one C substitution is solely the reason. The present work also shows that BRH is an inexpensive, promising and alternate candidate for n-C and n-SiC.

### 4.6: Codoped MgB\(_2\): An effective method for enhancing the in-field critical current density of MgB\(_2\)

#### 4.6.1: Introduction

Based on the nature of the dopant/additive, it can cause substitution at Mg/B site, or react with Mg/B to form reacted secondary phases or can be
incorporated in the superconductor matrix as inclusions without any chemical reaction. Addition of carbon containing compounds causes substitution of C at B site in the boron planes which modifies the \( \sigma \) and \( \pi \) band scattering and enhances the \( H_{C2} \) of MgB\(_2\) significantly. The lattice distortions, defects and strains caused by C substitution improve the flux pinning strength and in-field critical current density. From the comparative study of carbon variants (as described in section 4.5), n-C, n-SiC and BRH doped MgB\(_2\) samples are found to exhibit enhanced flux pinning and \( J_C \) both at lower and higher fields, competitively. Besides these carbon variants, addition of nano oxides such as Tb\(_4\)O\(_7\), Ho\(_2\)O\(_3\) and SiO\(_2\) are also found to increase flux pinning and critical current considerably, as seen in section 4.4. Of these, Ho\(_2\)O\(_3\) causes the formation of HoB\(_4\) as the reacted impurity phase, which interacts more strongly with the flux lines. Hence, n-Ho\(_2\)O\(_3\) doped sample exhibits better flux pinning behavior and thereby \( J_C(H) \) performance.

Based on these results, the combined effect of carbon variants and n-Ho\(_2\)O\(_3\) on the structural and superconducting properties of MgB\(_2\) is investigated in this section. Since these nano dopants have entirely different reaction/flux pinning mechanisms operative in MgB\(_2\), it is interesting to compare their effects on the structural and superconducting properties of MgB\(_2\). Our results show that the codoped samples have an additive effect of both the dopants on the superconducting performance of MgB\(_2\). Polycrystalline MgB\(_2\), (MgB\(_2\)+BRH+n-Ho\(_2\)O\(_3\)) and (MgB\(_2\)+n-SiC+n-Ho\(_2\)O\(_3\)) samples were prepared by \textit{in situ} PIST method using Mg, B, n-Ho\(_2\)O\(_3\), n-SiC and BRH as the starting materials. The details of sample preparation and characterizations are discussed in the previous sections. The MgB\(_2\) samples pure, (MgB\(_2\)+n-Ho\(_2\)O\(_3\)), (MgB\(_2\)+BRH), (MgB\(_2\)+n-SiC), (MgB\(_2\)+n-Ho\(_2\)O\(_3\)+BRH) and (MgB\(_2\)+n-Ho\(_2\)O\(_3\)+n-SiC) are named as MB, MBHo, MBR, MBS, MBHR and MBHS respectively.

**4.6.2: Results and discussion**

The XRD patterns of pure and codoped MgB\(_2\) samples are shown in figure 4.18. In the case of pure MgB\(_2\), all characteristic peaks are obtained with a trace amount of MgO. The MgO formation is due to the entrapped air
before the end sealing of the tubes and it slightly increases with the addition of BRH and n-Ho$_2$O$_3$. Mg$_2$Si phase is formed in MBHS which confirms the dissociation of SiC and it is consistent with the result obtained for monodoping of n-SiC. The dissociated Si reacts with Mg to form Mg$_2$Si and the free C is incorporated into the MgB$_2$ lattice. In MBHR sample, XRD pattern also shows Mg$_2$Si and MgO as main impurity phases wherein the MgO content is much higher compared to the other doped samples. Hence, it is clear that SiO$_2$ contained in BRH reacts with Mg to form Mg$_2$Si and MgO and the remaining C substitutes at B site. The presence of HoB$_4$ phase and the absence of residual Ho$_2$O$_3$ in both MBHR and MBHS indicate that the added Ho$_2$O$_3$ completely decomposes and reacts with B to form HoB$_4$. The codoped samples show both the reacted phases Mg$_2$Si and HoB$_4$ and these are found to have significant role in the enhancement of the flux pinning property of MgB$_2$.

![Figure 4.18: XRD patterns of pure and codoped MgB$_2$ samples](image)

It is clearly observed that the position of (110) peak slightly shifts to higher angles for codoped samples, indicating a decrease in the lattice parameter $a$. While, there is no shift in the (002) peak of any of the samples suggesting that there is no measurable change in the lattice parameter $c$. This means that the lattice parameter $c$ does not vary significantly within the
range of dopants studied, but the lattice parameter $a$ decreases. The lattice parameter $a$ of MgB$_2$ and its doped variants are calculated and tabulated in table 4.4. Compared to pure sample lattice parameter $a$ is found to be decreasing for all the codoped samples. The decrease of $a$ is an indication of the C substitution at B site which is further proved by the depression of $T_c$ in codoped samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Lattice parameters (nm)</th>
<th>FWHM (degree)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>$a$</td>
<td>$c$</td>
</tr>
<tr>
<td>MB</td>
<td>0.3087</td>
<td>0.3519</td>
</tr>
<tr>
<td>MBHR</td>
<td>0.3078</td>
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</tr>
<tr>
<td>MBHS</td>
<td>0.3073</td>
<td>0.3515</td>
</tr>
</tbody>
</table>

From the XRD, typical FWHM values of the MgB$_2$ peaks which represent peak broadening are given in table 4.4. The X-ray peak broadening is influenced by both crystallite size and lattice strain. The FWHM of all the codoped samples are found to be broadened as compared to pure MgB$_2$ sample. As in the case of lattice parameter $a$, here also C substitution has dominant role in enhancing the peak broadening. Since (100) and (110) peaks reflect the in-plane lattice constant of honeycomb boron lattice, the broadening of these peaks suggests the occurrence of some distortion in the lattice as a result of C substitution at B site. As the honeycomb boron lattice is responsible for superconductivity in MgB$_2$, the distortion results in the impurity induced scattering of charge carriers and thus enhances critical field through a reduction of coherence length.

To analyze the effect of grain size on peak broadening and observe the morphological features, microstructural examination was carried out using SEM. Figure 4.19 (a) and (b) shows the SEM images of the fractured surfaces of the MBHR and MBHS codoped samples. These samples show similar microstructure with randomly oriented and tightly packed flaky hexagonal grains. Figure 4.19 (c) and (d) show the TEM images of these
samples. The impurities in these codoped samples are clearly visible and are
distributed within the MgB$_2$ grains. These nano size (~20 nm) impurities
with size comparable to the coherence length of MgB$_2$ can pin the flux lines
within the grains.

Figure 4.19: (a)-(b) SEM and (c)-(d) TEM images of codoped MgB$_2$

Figure 4.20: Temperature dependence of DC magnetization plots for pure and codoped
MgB$_2$ samples
Temperature dependence of zero field cooled magnetization values for the undoped and codoped samples are shown in figure 4.20. Table 4.5 shows a comparison of superconducting properties of pure, monodoped and codoped MgB$_2$ samples. All the doped samples show a reduction in $T_C$ as compared to pure sample. C substitution together with the presence of non-superconducting phases decreases the $T_C$ in doped samples, while for MBHo sample the presence of reacted phase alone is the reason for $T_C$ reduction. The $\Delta T_C$ of superconducting transition of all the samples are also tabulated. The comparatively higher $\Delta T_C$ of MBS indicates that both C substitution due to SiC addition and the presence of non-superconducting reacted phases such as Mg$_2$Si reduce crystallinity and sample homogeneity.

Table 4.5: Comparison of superconducting properties of pure, monodoped and codoped MgB$_2$

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_C$ (K)</th>
<th>$\Delta T_C$ (K)</th>
<th>$J_C$ (A/cm$^2$) at 5 K</th>
<th>$F_{pmax}$ (GN/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>4 T ($\times 10^4$)</td>
<td>8 T ($\times 10^3$)</td>
</tr>
<tr>
<td>MB</td>
<td>38.6</td>
<td>1.0</td>
<td>1.4</td>
<td>0.1</td>
</tr>
<tr>
<td>MBHo</td>
<td>38.1</td>
<td>1.0</td>
<td>3.5</td>
<td>0.1</td>
</tr>
<tr>
<td>MBR</td>
<td>37.7</td>
<td>1.0</td>
<td>5.2</td>
<td>4.0</td>
</tr>
<tr>
<td>MBS</td>
<td>35.8</td>
<td>2.1</td>
<td>3.6</td>
<td>4.9</td>
</tr>
<tr>
<td>MBHR</td>
<td>37.6</td>
<td>1.2</td>
<td>8.4</td>
<td>7.2</td>
</tr>
<tr>
<td>MBHS</td>
<td>37.0</td>
<td>1.7</td>
<td>9.3</td>
<td>10.1</td>
</tr>
</tbody>
</table>

The magnetic field dependence of $J_C$, calculated from magnetic hysteresis measurements at 5 K is illustrated in figure 4.21. For the undoped sample, $J_C$ drops rapidly in the presence of magnetic field but for doped samples $J_C(H)$ behavior is significantly enhanced with respect to the pure sample throughout the entire range of field studied. Of all the doped samples, the codoped samples MBHR and MBHS give the best performance and the level of $J_C$ enhancement is around two times greater than their corresponding monodoped sample at 5 K and 8 T. The monodoped n-Ho$_2$O$_3$
Figure 4.21: $J_c(H)$ curves of pure, monodoped and codoped MgB$_2$ samples

Figure 4.22: $F_r(H)$ curves for the pure, monodoped and codoped MgB$_2$ samples
itself exhibits enhanced in-field $J_C$ compared to pure sample. The contribution towards the $J_C$ enhancement of n-SiC and BRH monodoped samples, comes partly from C substitution and partly due to the presence of reacted phases as flux pinners. For the codoped sample MBHS, both these effects, i.e. substitution due to C and flux pinning due to the reacted phases like Mg$_2$Si and HoB$_4$ contribute to the strong enhancement of $J_C$. Combined addition of n-Ho$_2$O$_3$ with BRH is also found to be much effective for the enhancement of $J_C(H)$ of MgB$_2$ than the solo addition of any one of the additives. The substitution of C at B site by BRH and the formation of magnetic particles of HoB$_4$ by Ho$_2$O$_3$ are the reasons for the strong improvement of $J_C(H)$ in this sample.

*Figure 4.22* shows the bulk $F_P(H)$ curves of the pure, monodoped and codoped MgB$_2$ samples. Since the flux jumps show significant marks on the shape of the $F_P(H)$ curves, the curves are plotted after refining the $J_C(H)$ data up to 2 T. It can be observed that the flux pinning behavior and $F_{P_{\text{max}}}$ values of all the doped samples have improved appreciably. Moreover, a peak shift of $F_{P_{\text{max}}}$ towards high field is observed for all the doped samples except MBHo. This is because all the doped samples except MBHo undergo C substitution at B site. At fields above $F_{P_{\text{max}}}$, both the codoped samples exhibit excellent flux pinning behavior due to the additive effect of n-Ho$_2$O$_3$ and corresponding carbon variants. From this, it can be concluded that combined addition of Ho$_2$O$_3$ with BRH and n-SiC was found to be much more effective than their solo addition for the enhancement in flux pinning and hence $J_C(H)$ performance of MgB$_2$.

### 4.6.3: Conclusion

The effect of combined addition of n-Ho$_2$O$_3$ with carbon variants, namely n-SiC and BRH on MgB$_2$ was investigated and its superconducting properties were compared to pure and its monodoped samples. The variations in both $a$ lattice parameter and FWHM imply that in codoped samples C is more effectively substituted at B site, which results local strains in MgB$_2$ lattice and the depression of $T_C$ also supports this. The $J_C(H)$ is significantly enhanced for all monodoped and codoped samples compared with the pure sample among which the codoped samples exhibit
the best performance in flux pinning and $J_C$ enhancement. The C substitution at B site by carbon dopants and the formation of Mg$_2$Si and magnetic particles like HoB$_4$ by Ho$_2$O$_3$ as flux pinners are the reasons for the strong improvement of $J_C(H)$ in these samples.

4.7: Summary

The influence of processing temperature and various nano dopants on the structural and superconducting properties of bulk MgB$_2$ superconductor prepared by in situ PIST method was studied. The samples heat treated at relatively lower temperatures particularly at 800 °C showed enhanced flux pinning as compared to those processed at higher temperatures. The reduced grain size and hence increased grain boundary is the main reason behind the improved flux pinning and $J_C(H)$ for the samples sintered at lower temperatures. In the comparative study of nano oxide doped MgB$_2$ samples, the $J_C(H)$ performance is significantly enhanced for all the doped samples. The addition induced reacted phases act as strong flux pinners thereby improving the $J_C(H)$ and $H_{irr}$ of the nano oxide doped samples. Flux pinning analysis also confirms the same, where n-Ho$_2$O$_3$ doped MgB$_2$ sample shows the maximum flux pinning behavior in the entire field of study because of the presence of magnetic impurities like HoB$_4$ as strong flux pinners. On comparing all the carbon variants doped samples, the n-C, n-SiC and BRH doped samples competitively exhibit highly enhanced $J_C(H)$. In the case of n-SiC and BRH doped samples, both C substitution and the presence of Mg$_2$Si cause enhanced flux pinning and hence $J_C(H)$ while for n-C doped one C substitution is solely the reason. The codoping of n-Ho$_2$O$_3$ with n-SiC and BRH exhibit excellent performance in flux pinning and $J_C$ enhancement up to a field of 8 T as compared to pure sample and their corresponding monodoped samples. The C substitution at B site by carbon dopants and the formation of Mg$_2$Si and magnetic particles like HoB$_4$ by Ho$_2$O$_3$ as flux pinners are the reasons for the strong improvement of $J_C(H)$ in these samples.
References:


