# Co-addition of nano-carbon and nano-silica: An effective method for improving the in-field properties of magnesium diboride superconductor

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## HIGHLIGHTS

- MgB$_2$ pure and doped with $n$-C, $n$-SiC and $n$-C + $n$-SiO$_2$ are prepared in bulk.
- Addition of $n$-SiO$_2$ with $n$-C improves carbon substitution.
- Co-doped sample exhibits enhanced critical current density in entire range of field.
- Uniformly distributed nano sized secondary phases provide additional flux pinning.

## ARTICLE INFO

## ABSTRACT

MgB$_2$ superconductor sample co-doped with nano-carbon ($n$-C) and nano-silica ($n$-SiO$_2$) is prepared and its structural and superconducting properties are compared with pure and $n$-C and nano SiC ($n$-SiC) mono-doped samples. Shrinkage of $a$-lattice parameter is observed for all doped samples, among which the co-doped sample exhibits the maximum shrinkage, an evidence of effective carbon substitution at boron sites. All doped samples show significantly enhanced in-field critical current density $J_C(H)$, where the co-doped sample dominates others throughout the whole range of field studied. Lattice strains induced by carbon substitution and flux pinning caused by uniformly distributed nano sized Mg$_2$Si particles formed by the reaction between Mg and $n$-SiO$_2$, are the main reasons for the highly enhanced $J_C(H)$ behavior of the co-doped superconductor.

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## 1. Introduction

The discovery of superconductivity in MgB$_2$ [1], with unusually high transition temperature (39 K) triggered an intense research around the world to make it useful for practical applications. The intrinsic properties such as simple crystal structure, low electromagnetic anisotropy, large coherence length and reasonable critical current density ($J_C$) [2,3] together with its low cost/performance ratio justify these efforts. The usefulness of a superconductor is determined by its ability to carry high current in high magnetic fields. Though MgB$_2$ possesses a self field $J_C$ of $10^5$–$10^6$ A cm$^{-2}$ at 4.2 K [4], it falls rapidly on application of high magnetic fields due to poor flux pinning ability and lower upper critical field ($H_{C2}$). Therefore, research is focused on to improve the in-field critical current density $J_C(H)$, $H_{C2}$ and irreversibility field ($H_{irr}$) of MgB$_2$ by enhancement of its flux pinning ability. Among the different methods used for these property improvement, chemical doping [5–17] is identified as the most convenient and effective method by researchers. Depending on the nature of dopants, chemical doping can cause defects and strains on crystal structure mainly by substitution of Mg and/or B by a third atom. Another approach is to create nano/submicron sized inclusions of reacted or unreacted phases within the grains of MgB$_2$. Both of these methods can improve the $H_{C2}$ and $H_{irr}$, and hence the $J_C(H)$. Among the various elements and compounds tried so far, carbon and carbon containing compounds such as $n$-C [5–7], carbon nanotubes [8], $n$-SiC [9–11], B$_4$C [12], BRH [13] and hydrocarbons [14–16] are found to be effective in enhancing the $J_C(H)$ to a significant level. While the

effectiveness of the substitution of boron atoms by carbon has made n-C a favorable dopant, carbon substitution and distribution of nanoscale reacted secondary phases in $MgB_2$ grains are the advantages of n-SiC. In addition to the carbon substitution, the size and amount of the additive and the homogeneity in distribution of the secondary phases also should be optimum for achieving enhanced flux pinning and hence improved $J_C(H)$ [15,17,18].

In the present work instead of using n-SiC as single dopant, co-doping of n-C and $n-SiO_2$ is carried out and the results are compared with those of pure and n-C and n-SiC independently doped samples. The doping level of carbon in all doped samples and all the processing parameters were kept identical for a meaningful comparison.

## 2. Experimental details

Polycrystalline samples with initial composition: $MgB_2$, $MgB_{1.9}C_{0.1}$, $MgB_2$ + 8.7 wt% n-SiC (8.7 wt% of SiC is equivalent to 0.1 atomic% of C in $MgB_2$) and $MgB_{1.9}C_{0.1}$ + 2.5 wt% $n-SiO_2$ were prepared by in situ Powder-In-Sealed-Tube (PIST) method using Mg (−325 mesh, 99.8%), amorphous B (−325 mesh, 99%), n-C (<50 nm, 99+%) n-SiC (<100 nm, 97.5%) and $n-SiO_2$ (10 nm, 99.5%) as starting powders. The stoichiometry of carbon was decided on the basis of a previous study [19]. Stoichiometrically weighed and homogeneously mixed powders were densely packed into stainless steel tubes of OD/ID = 10/8 mm with suitable length. Both the ends and the powder filled segment of the tubes were pressed using a hydraulic press in order to get a bar shaped sample. The ends of the pressed samples were sealed by arc welding in order to prevent oxidation of Mg during heat treatment. Samples were then heat treated in air at 850 °C for 2 h in a muffle furnace with a ramp rate of 5 °C min⁻¹. After heat treatment the reacted core was recovered by mechanically peeling off the stainless steel sheath. The structural and phase analysis of the samples were performed using X-ray Diffractometer (Philips X'pert Pro) with CuKα radiation employing a proprietary detector (X'Celerator) and a monochromator at the diffracted beam side. Phase identification of the samples was performed using X'Pert Highscore Software in support with ICDD-PDF-2 database. The grain morphology and microstructure were examined by a scanning electron microscope (JEOL JSM 5600 LV) and a high resolution transmission electron microscope (FEI-Tecnai $G^2$ 30 S-Twin 300 kV). DC magnetic measurements were carried out using a vibrating sample magnetometer (Quantum Design, USA) with bar shaped samples having size 1.5 mm × 3 mm × 3 mm.
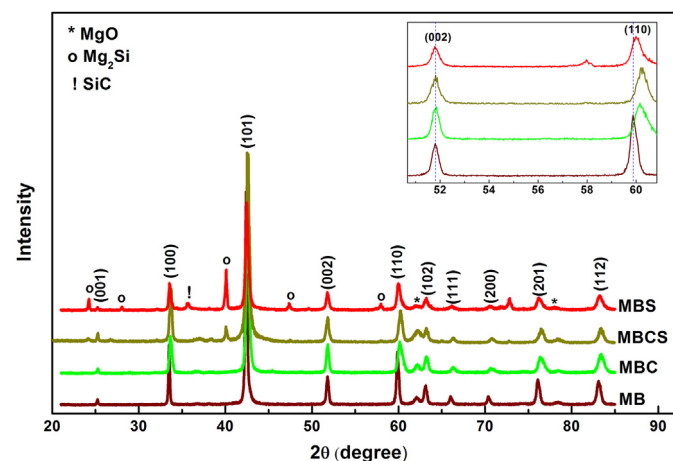
**Table 1**
Semi-quantitative phase analysis of different phases present in pure and doped samples.

| Sample | Initial composition | Vol% of different phases | | | |
|---|---|---|---|---|---|
| | | $MgB_2$ | MgO | $Mg_2Si$ | SiC |
| MB | $MgB_2$ | 98.1 | 1.9 | – | – |
| MBC | $MgB_{1.9}C_{0.1}$ | 96.2 | 3.8 | – | – |
| MBS | $MgB_2$ + 8.7 wt% n-SiC | 72.1 | 1.1 | 24.9 | 1.9 |
| MBCS | $MgB_{1.9}C_{0.1}$ + 2.5 wt% $n-SiO_2$ | 89.5 | 4.7 | 5.8 | – |

## 3. Results and discussion

Fig. 1 shows powder XRD patterns of pure and doped samples. The peaks of $MgB_2$ are indexed with corresponding planes of reflection. The semi quantitative phase analysis of different phases was done using the relation, *Vol% of phase X = Speak intensities of phase X/S peak intensities of all phases* and are tabulated in Table 1. The main phase in all samples is $MgB_2$, along with traces of MgO. The sample added with nano-C and $n-SiO_2$ (MBCS), shows higher amount of MgO compared to other samples. This is because besides the entrapped air contained in the precursor filled tubes, $n-SiO_2$ also acts as an oxygen source. Except MgO, no peaks of any other impurities are observed for pure (MB) and n-C doped (MBC) samples. The sample added with n-SiC (MBS) shows a significant amount of $Mg_2Si$ and minor quantities of unreacted SiC. The dissociation of SiC and reaction of Si with Mg to form $Mg_2Si$ start even at temperatures as below as 600 °C [18,20].The carbon atoms separated from SiC get substituted into $MgB_2$ lattice by replacing B atoms. Lower, but an observable amount of $Mg_2Si$ is present in the sample co-doped with n-C and $n-SiO_2$ (MBCS). Here the formation of $Mg_2Si$ is according to the chemical reaction $4Mg + SiO_2 \rightarrow Mg_2Si + 2MgO$. Since the atomic% of Si is lower in dopant of MBCS than that in MBS the vol% of $Mg_2Si$ is also lower in MBCS.

Inset of Fig. 1 shows an enlarged view of (0 0 2) and (1 1 0) peaks. The (1 1 0) peaks of all doped samples are shifted towards higher $2\theta$ values, an indication of a-axis shrinkage, but (0 0 2) peaks do not show appreciable shift from that of pure sample. The lattice parameters 'a' and 'c' were calculated and results are tabulated in table. Among the doped samples, MBCS shows the lowest value of a axis length and MBS the highest. Studies have already revealed that, when carbon atoms replaces boron atoms from $MgB_2$ lattice, having a hexagonal structure with B atoms forming a graphite like honeycomb network and Mg atoms occupying the pores of these hexagons, due to lower covalent radius of carbon, the in-plane lattice shrinks [21,22]. All doped samples undergo carbon substitution, of which the sample co-doped with $n-SiO_2$ shows the best result. Though the sample MBC is also added with same amount of carbon, it shows less carbon substitution than that of MBCS. So it is inferred that the addition of nano-$SiO_2$ with n-C causes better carbon substitution in $MgB_2$.

Table 2 shows the Full Width at Half Maximum (FWHM) values of (1 0 0), (1 0 1), (0 0 2) and (1 1 0) peaks. The FWHM of (0 0 2) peaks of the doped samples does not show significant variation



**Fig. 1.** XRD patterns of pure, mono-doped and co-doped $MgB_2$ samples. The inset shows an expanded view of the (0 0 2) and (1 1 0) peaks of all samples.

**Table 2**
FWHM values of (1 0 0), (1 0 1), (0 0 2), and (1 1 0) peaks of samples.

| Sample | FWHM of selected peaks | | | | |
|---|---|---|---|---|---|
| | 1 0 0 | 1 0 1 | 0 0 2 | 1 1 0 | 1 0 0 |
| MB | 0.188 | 0.273 | 0.318 | 0.315 | 0.188 |
| MBC | 0.349 | 0.423 | 0.340 | 0.583 | 0.349 |
| MBS | 0.285 | 0.369 | 0.350 | 0.482 | 0.285 |
| MBCS | 0.308 | 0.405 | 0.380 | 0.503 | 0.308 |