

# **Studies on development of MgB<sub>2</sub> superconductor with improved in-field critical current density**

Thesis submitted to  
Cochin University of Science and Technology (CUSAT)  
in partial fulfillment of the requirements for the award of the degree  
of  
**Doctor of Philosophy**  
in **Physics** under the **Faculty of Science**

by

**VINOD. K**

under the supervision of

**Dr. U. Syamaprasad**



**National Institute for Interdisciplinary Science and Technology**  
(Council of Scientific and Industrial Research)  
Thiruvananthapuram-695019  
January 2010

**Studies on development of MgB<sub>2</sub> superconductor  
with improved in-field critical current density**

Dedicated to

*my father, mother and brother*

## DECLARATION

I, Vinod. K., hereby declare that, this thesis entitled “**Studies on development of MgB<sub>2</sub> superconductor with improved in-field critical current density**” is a bonafide record of the research work done by me under the supervision and guidance of Dr. U. Syamasasad, Scientist, National Institute for Interdisciplinary Science and Technology (CSIR), Thiruvananthapuram and that no part of this thesis has been presented earlier for any degree, diploma, associateship, or any other title or recognition of any other University.

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**CERTIFICATE**

This is to certify that the thesis entitled “**Studies on development of MgB<sub>2</sub> superconductor with improved in-field critical current density**” is an authentic record on the research work carried out by Mr. Vinod. K., under my supervision in partial fulfillment of the requirement for the degree of **Doctor of Philosophy** of the Cochin University of Science and Technology and further that no part of this thesis has been presented for any other degree.

**U. Syamaprasad**

## Acknowledgments

During my last 5 years of research work at NIIST, for the Ph.D. degree, many people contributed to my research and life. I wish to express my sincere gratitude and appreciation to all those, whose contribution I value.

I am truly grateful to my supervisor, **Dr. U. Syamaprasad** for the guidance and encouragement. I sincerely thank him, for the support and opportunities he provided to me.

I sincerely appreciate the help and friendship of the entire Superconducting materials research group during my studies. In particular, I thank: **Mr. P Guruswamy**, for the technical support and encouragement; my colleagues, **S. Rahul, Neson Varghese, K. M. Devadas, Syju Thomas, P. M. Sarun, S. Vinu, R. Shabna, P. M. Aswathy, J. B. Anooja, K. T. Jakson, A. Sivaprakash, S. Santhosh Kumar and G. R. Anuraghi** for the help, friendship and fruitful scientific discussions. I specially thank **Dr. R. P. Aloysius** for the useful scientific discussions, support and help. I thank **Dr. A. Biju, R. G. Abhilash kumar and S. Thennavarajan** for the support and help. I also thank **B. Premalal** for sending me the journal articles I requested. I thank **M. Suresh, T. Antony Prabhu, A. Nazeer, A. Vasudevan, S. S. Soorya, C. Navya Paul, V. G. Prabitha and Rosamma Sebastian** for their help and friendship. Special thanks are due to **Mr. M. R. Chandran, Dr. Prabhakar Rao, Mr. Robert Philip, Mr. Narendran and Dr. V. S. Prasad** of *NIIST*, Trivandrum for performing the SEM, TEM and EDS of the samples.

I sincerely thank **Dr. A. Sundaresan**, *Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), Bangalore*, **Dr. S. B. Roy**, *Raja Ramanna Centre for Advanced Technology (RRCAT), Indore* and **Dr. S. Pradhan**, *Institute for Plasma Research (IPR), Gandhinagar*, for experimental support, fruitful scientific discussions and collaboration.

I also thank **Prof. Ashok Rao**, *Department of Physics, Manipal Institute of Technology, Manipal*, and **Prof. Y. K. Kuo**, *Department of Physics, National Dong Hwa University, Hualien, Taiwan*, for experimental support.

I thank **Dr. Suresh Das**, *Director, NIIST*, **Dr. B. C. Pai** and **Prof. T. K. Chandrasekhar**, *former Directors of NIIST*, for providing all the facilities

to carry out this work and for their encouragement during this work. I thank **Dr. K. G. K. Warriar**, *Head, Materials Division, NIIST* for the support and encouragement. I also thank **Prof. K. P. Vijayakumar**, *Department of Physics, Cochin University of Science and Technology, Kochi* for useful discussions at various stages of the work.

I sincerely acknowledge the *Council of Scientific and Industrial Research (CSIR)* for providing the research fellowship and thus an opportunity to do the present work.

Vinod. K

## PREFACE

In the superconducting state, a superconductor has zero electrical resistance and hence can transport large electrical currents without any resistive loss. The unique property of dissipation free current transport has strong prospective on practical applications. Today superconducting materials have extensive uses in energy production, storage and distribution, in electronics, and most importantly in high field magnets. Superconducting magnets have major use in MRI instruments in medical field, for high field R & D instruments like NMR, for energy storage in SMES, for confinement of plasma in fusion reactors and for the magnetic levitation systems in transportation. The wide spread use of superconductors is mainly limited by cost associated with maintaining very low temperatures.

The most commonly used superconducting materials are two low temperature superconductors (LTS), NbTi having a  $T_C$  of 9 K and Nb<sub>3</sub>Sn having a  $T_C$  of 18 K. NbTi has an  $H_{C2}$  of 10-11 T at 4.2 K and is relatively easy to fabricate in wires or tapes and occupies most of the low field magnets in MRI instruments. Nb<sub>3</sub>Sn has  $H_{C2}$  value of more than 20 T at 4.2 K and is used in high field magnets. Both NbTi and Nb<sub>3</sub>Sn based magnets use liquid helium (LHe) as the coolant, which is expensive. The discovery of high temperature superconductors (HTS), superconducting above 77 K and having  $H_{C2}$  more than 100 T, made excitement with the possibility of operating superconducting devices at a reduced cost. These can be cooled to the superconducting state using liquid nitrogen (LN<sub>2</sub>), which is much cheaper than liquid helium. But the HTS conductors faced many technical problems in making wires and coils. These materials are granular and highly anisotropic and the critical current density falls sharply in applied fields.

The discovery of superconductivity in MgB<sub>2</sub>, a binary intermetallic, in 2001 by Jun Akimitsu's group in Japan generated a boom in applied superconductivity research. MgB<sub>2</sub> has a higher  $T_C$  of 39 K as compared to the conventional LTS and is free from most of the limitations of HTS. MgB<sub>2</sub> conductors with large transport current densities of around  $10^5$  A/cm<sup>2</sup> at 4.2-20 K have been demonstrated in a few labs. MgB<sub>2</sub> based systems can be operated in the 20-30 K temperature range with cryocoolers (eliminates the need for expensive LHe), where conventional LTS cannot be used. Compared to the HTS, preparation of MgB<sub>2</sub> into multifilamentary conductors is relatively easy and the raw materials are inexpensive.

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Currently the major challenges involved in the development of  $\text{MgB}_2$  conductors for practical applications are the preparation of good quality  $\text{MgB}_2$  in bulk, wire/tape and coil, and improvement of field performance. The oxidation and vapor loss of Mg are the main hurdles for the preparation of good quality  $\text{MgB}_2$ . The wide difference in the melting point between Mg (650 °C) and B (2080 °C) limits the solid - solid and liquid - liquid reaction, and the  $\text{MgB}_2$  formed by liquid - solid reaction is highly porous. The sinterability of  $\text{MgB}_2$  grains is poor also. Mg reacts with most of the common sheath metals and the mechanical workability of chemically compatible metals is low.  $\text{MgB}_2$  has high critical current density at self-field, but the critical current density falls sharply in applied fields. For technological applications the in-field critical current density must be improved considerably.

The present thesis focuses on the preparation of good quality  $\text{MgB}_2$  in bulk, wire/tape forms and on the improvement of in-field critical current density. The results can be used for the development of  $\text{MgB}_2$  based superconductors for practical applications.

The thesis is organized into 6 chapters. First chapter gives a brief introduction to the phenomenon of superconductivity, superconducting materials, applications and the features of  $\text{MgB}_2$  superconductor. A review of the present international status on the development of  $\text{MgB}_2$  is also given in the chapter. The second chapter discusses the various material characterization techniques used for the study. Third, fourth and fifth chapters describes the experimental results, main findings and discussion of the research carried out. Third chapter deals with the preparation and characterization of bulk  $\text{MgB}_2$  superconductor. Fourth chapter deals with the preparation and characterization  $\text{MgB}_2$  superconductor in mono and multifilamentary wire/tape form. Fifth chapter deals with the chemical addition studies carried out to improve the in-field critical current density of  $\text{MgB}_2$  superconductor. Chapter 6 summarizes the work with main conclusions and the scope for future work.

A simple Powder-In-Sealed-Tube (PIST) method is identified for preparing good quality  $\text{MgB}_2$  bulk superconductor. In this method, Mg and B powders were filled in seamless stainless steel tubes and heat treated in atmospheric condition after sealing the ends. The method is simple and cost effective, as the need for vacuum or inert atmosphere is eliminated for the

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preparation. For the preparation of wires and tapes a systematic study on the chemical reactivity of various sheath materials such as Ag, Cu, Fe, Ni, Stainless Steel (SS) and Ta with Mg/B was conducted. Among these Fe is found to be the most suitable material for the sheath. Fe sheathed MgB<sub>2</sub> wires and tapes were prepared by *in situ* Powder-In-Tube (PIT) technique in mono and multi filamentary geometries. Further, a novel electrical self-heating method was introduced for the preparation of Fe sheathed MgB<sub>2</sub> wires and tapes. The prepared superconductor in bulk, wire and tape forms were characterized for phase purity, structural and superconducting properties, and these are at par with the best quality samples reported worldwide.

Additives of different types were introduced into the MgB<sub>2</sub> for improving the in-field critical current density. Burned rice husk (BRH), an inexpensive natural material is found to be one of the best additive for enhancing the in-field critical current density of MgB<sub>2</sub>. By selecting suitable combinations of additives a significant enhancement of the critical current density by 1-2 orders of magnitude were achieved for fields > 5 T, at 5 and 15 K.



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## Details of patents and publications

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### List of patents granted/filed

**Title: A process for continuous production of Magnesium Diboride based superconductors**

U. Syamaprasad, R. G. Abhilash Kumar, **K. Vinod**, R. P. Aloysius, P. M. Sarun, S. Thennavarajan, P. Guruswamy

1. US patent (granted): Patent no US 7456134 B2
2. UK patent (filed): 0185NF2005/GB, filing date: 23-04-2008
3. German patent (filed): 0185NF2005/DE, filing date: 21-05-2008
4. Japan patent (filed): 0185NF2005/JP, filing date: 26-05-2008
5. Indian patent (filed): 0185NF2005/IN, filing Date: 25-11-2005

### List of papers published in SCI journals

1. Highly enhanced in-field critical current density of MgB<sub>2</sub> superconductor by combined addition of burned rice husk and nano Ho<sub>2</sub>O<sub>3</sub>  
**K. Vinod**, Neson Varghese, A. Sundaresan and U. Syamaprasad, accepted for publication in *Solid State. Sci.*
  2. Effect of combined addition of nano SiC and nano Ho<sub>2</sub>O<sub>3</sub> on the in-field critical current density of MgB<sub>2</sub> superconductor  
Neson Varghese, **K. Vinod**, M. K. Chattopadhyay, S. B. Roy and U. Syamaprasad, *J. Appl. Phys.* 107 (2010) 013907(1-5)
  3. Burned rice husk: An effective additive for enhancing the electromagnetic properties of MgB<sub>2</sub> superconductor  
Neson Varghese, **K. Vinod**, Shipra, A. Sundaresan and U. Syamaprasad *J. Am. Ceram. Soc.* DOI: 10.1111/j.1551-2916.2009.03438.x
  4. Significant enhancement of the in-field critical current density of the MgB<sub>2</sub> superconductor through codoping of nano-TiC with nano-SiC  
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9. Prospects of MgB<sub>2</sub> superconductors for magnet application  
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**K. Vinod**, Neson Varghese, S. Rahul and U. Syamaprasad communicated to *J. Natural Sciences.* [Invited paper]

## List of papers presented/published in seminars/conferences

1. Studies on development of MgB<sub>2</sub> superconductor with improved in-field critical current density. [Invited paper]  
**K. Vinod** and U. Syamaprasad, Presented at the DST-JSPS Asia Science Seminar held at Yokohama, Japan on December 8-15, 2009.

2. Combined effect of burned rice husk and nano  $\text{Ho}_2\text{O}_3$  on the in-field critical current density of  $\text{MgB}_2$  superconductor.  
S. Rahul, G. R. Anuraghi, K. T. Jakson, Neson Varghese, **K. Vinod** and U. Syamaprasad, Presented at the International Conference on Advanced Functional Materials (ICAFM 2009), held at NIIST, Trivandrum on December 09-10, 2009.
  3. Effect of combined addition of nano SiC and TiC on the structural and superconducting properties of  $\text{MgB}_2$ .  
Neson Varghese, J. B. Anooja, P. M. Aswathy, **K. Vinod**, S. B. Roy and U. Syamaprasad, Presented at the International Conference on Advanced Functional Materials (ICAFM 2009), held at NIIST, Trivandrum on December 09-10, 2009.
  4. Hot pressing of electrically self-heated  $\text{MgB}_2/\text{Fe}$  PIT wires.  
**K. Vinod**, Neson Varghese, S. Rahul and U. Syamaprasad, Presented at the 53<sup>rd</sup> DAE Solid State Physics Symposium (DAE SSPS 2008), held at BARC on December 16-20, 2008. (Also published in the proceedings: vol 53 page 919-920)
  5. Enhancement of high field critical current density in nano SiC doped  $\text{MgB}_2$  prepared by powder-in-sealed-tube method.  
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  6. Synthesis of  $\text{MgB}_2$  superconductor by an electrical self-heating method  
**K. Vinod**, R. G. Abhilash Kumar, R. P. Aloysius and U. Syamaprasad, Presented at the 18<sup>th</sup> AGM, Materials Research Society of India (MRSI), held at NPL NewDelhi on February 12-14, 2007
  7. Influence of heat treatment temperature and duration on the crystalline and microstructural properties of *in situ*  $\text{MgB}_2$  superconductor  
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  8. Chemical compatibility of sheath materials for *in situ*  $\text{MgB}_2$  superconductor wire/tape fabrication  
Neson Varghese, **K. Vinod**, R. G. Abhilash Kumar and U. Syamaprasad, Presented at the International Conference on Advanced Materials and Composites (ICAMC), held at NIIST Thiruvananthapuram on October 24-26, 2007. (Also published in the proceedings: page 773-778)
  9. Effect of sintering temperature on the microstructure and superconducting properties of *in situ* polycrystalline  $\text{MgB}_2$   
**K. Vinod**, Neson Varghese and U. Syamaprasad, Presented at the 52<sup>nd</sup> DAE Solid State Physics Symposium (DAE SSPS 2007), held at Mysore on December 27-31, 2007. (Also published in the proceedings: vol 52 page 791-792)
  10. Structural and superconducting properties of  $\text{MgB}_2$  added (Bi,Pb)-2212 superconductor  
R. G. Abhilash Kumar, **K. Vinod**, A. Biju and U. Syamaprasad, Presented at the XXVIII National Conference on Electrom Microscopy Society of India, April 19-21, 2006
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# List of Abbreviations

at.%	Atomic percentage
wt.%	Weight percentage
Vol.%	Volume percentage
LTS	Low Temperature Superconductor
HTS	High Temperature Superconductor
BCS	Bardeen Cooper and Schrieffer
ZFC	Zero Field Cooling
FC	Field Cooling
MRI	Magnetic Resonance Imaging
NMR	Nuclear Magnetic Resonance
FCL	Fault Current Limiter
SMES	Superconducting Magnetic Energy Storage
XRD	X-Ray Diffraction
SEM	Scanning Electron Microscopy
SEI	Secondary Electron Imaging
TEM	Transmission Electron Microscopy
EDS	Energy Dispersive X-Ray Spectrum
FWHM	Full Width at Half Maximum
RRR	Residual Resistivity Ratio
SQUID	Superconducting QUantum Interference Device
VSM	Vibrating Sample Magnetometer
PPMS	Physical Property Measurement System
PIT	Powder In Tube
PIST	Powder In Sealed Tube
RE	Rare Earth
REO	Rare Earth Oxide
BRH	Burned Rice Husk
CNT	Carbon Nano Tube
LN <sub>2</sub>	Liquid Nitrogen
LHe	Liquid Helium
HIP	Hot Isostatic Pressing
HPS	High Pressure Sintering
DOS	Density of States
DFT	Density Functional Theory
ICDD	International Center for Diffraction Data
PDF	Powder Diffraction File
DC	Direct Current
AC	Alternating Current
PC	Personal Computer
GPIB	General Purpose Interface Board



SS	Stainless Steel
OD	Outside Diameter
ID	Inside Diameter
NIIST	National Institute for Interdisciplinary Science and Technology
SW	Mono (Single) filamentary wire
ST	Mono (Single) filamentary tape
MW	Multifilamentary wire
MT	Multifilamentary tape
JNCASR	Jawaharlal Nehru Centre for Advanced Scientific Research
RRCAT	Raja Ramanna Centre for Advanced Technology
IPR	Institute for Plasma Research

# List of Symbols

a, b, c	Sample dimensions
$a, c$	Lattice parameters
$d$	Inter atomic spacing
$h, k, l$	Miller indices of crystal planes
$\text{\AA}$	Angstrom unit
T	Temperature
I	Current
V	Voltage
M	Magnetization
H	Magnetic field
R	Resistatnce
$\rho$	Resistivity
$\chi$	Magnetic Susceptibility
$T_C$	Critical temperature (Transition temperature)
$T_{\text{Conset}}$	Temperature corresponding to Onset of transition
$T_{\text{Coffset}}$	Temperature corresponding to Offset of transition
$\Delta T_C$	Width of Transition (Difference between and $T_{\text{Conset}}$ and $T_{\text{Coffset}}$ )
$I_C$	Critical Current
$J_C$	Critical Current density
$J_E$	Engineering Critical Current density
$J_C(H)$	In-field Critical Current density
$H_C$	Critical Field
$H_{C1}$	Lower Critical Field
$H_{C2}$	Upper Critical Field
$H_{\text{irr}}$	Irreversibility Field
$F_P$	Flux pinning force density
$F_{P\text{max}}$	Maximum flux pinning force density
$H_{\text{peak}}$	Field corresponding to maximum flux pinning force density
$\xi$	Coherence length
$\lambda$	Penetration depth
$\sigma$	$\sigma$ Bonding
$\pi$	$\pi$ Bonding
$\Delta(0)$	BCS energy gap at 0 K
$\Delta_\sigma$	$\sigma$ band energy gap
$\Delta_\pi$	$\pi$ band energy gap
$\mu^*$	Chemical potential

# Chapter 1

## Introduction to $\text{MgB}_2$ superconductor

### 1.1 Superconductivity

In 1908 Heike Kamerlingh Onnes, professor of experimental physics at the university of Leiden (Holland) liquified helium for the first time. He soon set about measuring the electrical resistivity of metals at low temperatures. In 1911, while measuring the electrical resistivity of mercury, he observed a sudden and massive drop in resistivity below 4.2 K. As the mercury wires were slowly cooled below 4.2 K, in just a few hundredths of a degree, the resistance dropped to immeasurably low value. i.e. practically into zero [1]. Onnes termed the electrical state mercury had entered as **superconducting** state. Thus the phenomenon of vanishing of electrical resistivity of materials below a particular low temperature has been called **superconductivity** and the materials which exhibit this property are called **superconductors**. The temperature at which the transition from normal state to superconducting state occurs is called the superconducting transition temperature or **critical temperature**  $T_C$ .

In 1933 Meissner and his student Robert Oschenfeld made an important discovery about the behavior of superconductors in external magnetic fields. While investigating the superconducting transition of materials in applied magnetic fields, they found that the magnetic flux was expelled from the interior of the superconductor (for field upto a critical field  $H_C$ ),

irrespective of the path used to apply the field [2]. This characteristic property of a superconductor is called the **Meissner effect**. The complete expulsion of magnetic flux shows that the superconductor is perfectly diamagnetic in the superconducting state.

The normal and superconducting state of a material is determined by the temperature, external magnetic field and the current density flowing through the material. Thus for the occurrence of superconductivity in a material the temperature must be below the **critical temperature** ( $T_C$ ), the external magnetic field must be below the **critical field** ( $H_C$ ) and the current density flowing through the material must be below the **critical current density** ( $J_C$ ). The three parameters  $T_C$  ( $H, J$ ),  $H_C$  ( $T, J$ ) and  $J_C$  ( $H, T$ ) define a critical surface as illustrated in figure 1.1, beneath the surface the material is in superconducting state and above the surface the material is in normal state.

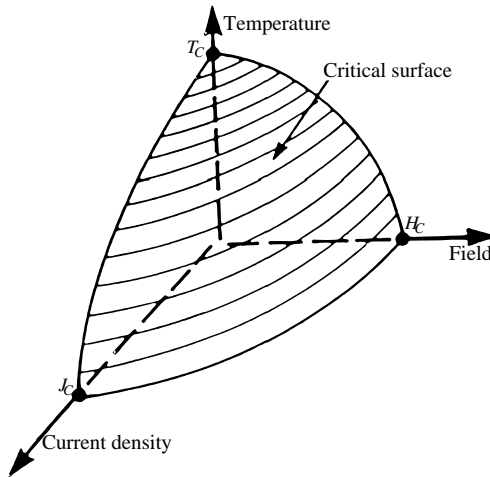


Figure 1.1: Illustration of superconducting critical surface.

The usefulness of a superconductor for technological applications depends on its ability to carry sufficient high current density without resistive losses at the working field ( $H$ ) and temperature ( $T$ ). There are two limits to the  $J_C$  in practical superconductors: the intrinsic  $J_C$  is limited by  $H_{C2}$ ,  $H_{IT}$

and flux pinning, and the extrinsic  $J_C$  limited by factors like grain connectivity, grain orientation (anisotropy). One of the aims of the present work is to improve the  $J_C$  of MgB<sub>2</sub> superconductor at higher fields by selective chemical addition.

## 1.2 Electromagnetic properties of superconductors

Superconductors have peculiar electromagnetic properties that differ very much from that of normal conducting materials. In the superconducting state a superconductor has zero electrical resistance and can carry DC transport currents without any dissipation or energy loss, upto the critical current ( $I_C$ ). The behavior of a superconductor in an AC field or AC transport current is more complex and is not included in the discussion as it is outside the scope of the present work. In the case of AC transport currents, the flow is superconducting at lower frequencies, the current experiences an inductive reactance at higher frequencies. At optical frequencies ( $> 10^{14}$  Hz), the AC current flow is mostly normal.

A superconductor behaves differently from that of a normal conductor in an external magnetic field. Based on their behavior in an external field, superconductors are classified into two categories – Type I and Type II superconductors.

In the superconducting state a superconductor shows Meissner effect and expels an external magnetic field from its interior, upto a **thermodynamic critical field**  $H_C$ . The expulsion of field is independent of the experimental history ie. whether the field is applied after cooling below  $T_C$  (Zero Filed Cooling – ZFC) or the superconductor is cooled below the  $T_C$  in the presence of a field (Field Cooling – FC). While the description of the field being excluded from the volume is reasonable, in reality the external field penetrates to a small depth, to the so called London penetration length  $\lambda = \frac{m_e}{\sqrt{\mu_0 n_s e^2}}$ , where e and  $m_e$  are the charge and mass of electron and  $n_s$  is the density of superconducting electrons. Inside the superconductor, the density of superconducting electrons cannot change abruptly and changes gradually only over a distance called the coherence length  $\xi$ . That is there is no sharp boundary between a normal conducting and superconducting regions and the transition from a superconducting to normal conducting

region takes place over a length of  $\xi$ . The coherence length has a constant value at the core of a superconducting region and decreases gradually to zero at the interface of normal region. The ratio of penetration depth to the coherence length of a material is known as the Ginsburg-Landau constant  $K$  ( $K = \frac{\lambda}{\xi}$ ). A material is a type I superconductor for the Ginsburg-Landau constant  $K = \frac{\lambda}{\xi} < \frac{1}{\sqrt{2}}$  and a type II superconductor for  $K = \frac{\lambda}{\xi} > \frac{1}{\sqrt{2}}$  [3, 4, also page 19-20 of ref:12].

### 1.2.1 Type I superconductors

Type I superconductors expel an external magnetic field from their interior, upto a thermodynamic **critical field**  $H_C$ . For external fields above  $H_C$  the superconductor turns into normal material and allows the external fields to penetrate to the interior of the superconductor. For fields  $< H_C$  (Meissner state) Type I superconductor acts as a perfect diamagnet so that  $\chi = -1$  and  $M = -H$  and for fields  $> H_C$  (normal state)  $\chi = 0$  and  $M = 0$ . Figure 1.2 (a) shows the variations of internal field with external field for a type I superconductor.

### 1.2.2 Type II superconductors

Below a **lower critical field**  $H_{C1}$ , a type II superconductor behaves as that of a type I superconductor and expels any magnetic field from its interior. For fields above the  $H_{C1}$  the external magnetic field starts to penetrate into the interior of the type II superconductor in the form of quantized flux vortices. These quantized flux vortices are known as fluxons and each fluxon is a tube of radius of the London penetration depth  $\lambda(T)$  in which superconducting screening currents circulate around a small non superconducting core of radius  $\xi(T)$ . The flux carried by a single fluxon is  $\Phi_0 = \frac{h}{2e} = 2 \times 10^{-15}$  Wb [3, 4]. As the external field increases, more and more flux vortices are created at the surface of the superconductor and are penetrated into the interior, and they arrange themselves in a regular lattice. This state, called the mixed state or **vortex state** is important for the practical applications. As the fields increases further, the flux vortices fill the superconducting matrix and thus reduce the superconducting area. At a particular high field, called the **upper critical field**  $H_{C2}$ , the entire superconducting area is filled by vortices and the superconductor turns into a normal material. For fields  $< H_{C1}$  (Meissner state) type II superconductor acts as a perfect diamagnet so that  $\chi = -1$  and  $M = -H$ , for fields  $> H_{C1}$  and  $< H_{C2}$  (mixed or vortex state) magnetic field penetrates in the form of

quantized vortices so that  $0 > \chi > -1$  and  $0 > M > -H$  and for fields  $> H_{C2}$  (normal state)  $\chi = 0$  and  $M = 0$ . Figure 1.2 (b) shows the variations of internal field with external field for a type II superconductor. Figure 1.2 (c) and (d) show schematic H–T phase diagrams for type I and type II superconductors respectively. The  $H_{C1}$  is of order of 10–100 mT for most of the type II superconductors, while they have very high  $H_{C2}$  values of several tesla.

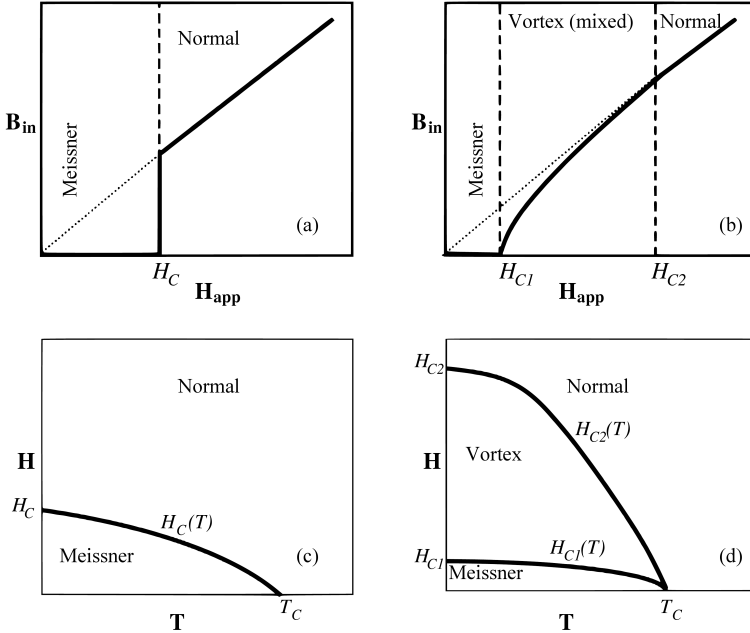


Figure 1.2: Variation of internal field with external field for (a) type I and (b) type II superconductor. (c) and (d) shows the H-T phase diagram of type I and type II superconductor.

### 1.2.3 Vortex (mixed) state of Type II superconductors: Flux pinning and critical current density

For a type II superconductor, in the vortex state the superconductor is filled with fluxons. These fluxons have a normal core of quantized magnetic field lines. The number of quantized vortices increases with external field and in

a perfect superconducting crystal the competition between the inter-vortex repulsion and the magnetic pressure from the outside field causes the vortices to arrange themselves in a regular lattice. But in real superconductors there are defects, which pin the vortices, and stop from moving, disrupting the Flux Line Lattice (FLL) [4, 5]. But with increasing temperature ( $T$ ) and field ( $H$ ) the flux lines attain enough energy to depin from the pinning sites and start to migrate to form FLL. Figure 1.3 shows a schematic diagram of vortex state of a type-II superconductor.

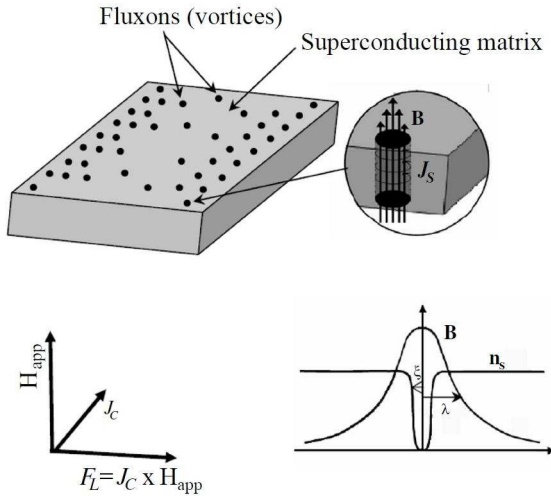


Figure 1.3: Type II superconductor in the vortex state, showing flux vortices and the variation of superconducting electron density ( $n_s$ ), and the field ( $B$ ) in a vortex core.  $J_S$  is the superconducting circulating screening currents associated with the vortices.

During a macroscopic transport current flow through the superconductor, the fluxons experience a Lorentz force  $F_L = J_C \times B$ , in a direction perpendicular to both the current density and field. This Lorentz force tends to move the flux lines. The lattice defects or imperfections can pin the flux lines to some extent and once the Lorentz force exceeds this pinning force, the flux lines start to move. The flux lines experience some viscous resistance in their movement and cause energy dissipation in the superconductor. The flux flow induces an electric field  $E = n_f \Phi_0 \nu_f$  (where  $n_f$  is the number of fluxons,  $\Phi_0$  is the quantum of flux and  $\nu_f$  is the veloc-



ity of flux flow) and the transport current becomes dissipative. The flux flow and dissipation are higher for increased temperature or applied field. This limits the non dissipative  $J_C(T, H)$  to a value, defined by the balance of the pinning and Lorentz forces [page 94-102 of ref:12 and chapter 9, page 303 of ref: 6]. Due to the flux flow, for an applied field above a limit, called the **irreversibility field**  $H_{irr}$ , (much below the upper critical field  $H_{C2}$ ) energy dissipation starts and hence dissipation free transport current flow stops. In order to sustain the non dissipative current flow at high fields and temperatures the flux lines must be pinned.

The physics and engineering of vortex dynamics and flux pinning are highly interesting and are active research fields in applied superconductivity. The atomic or crystal defects such as grain boundaries, voids, strains, twin planes, inhomogeneities and secondary phases present in real superconductors are effective pinning sites.<sup>1</sup> The flux pinning can be improved to maximize  $J_C$  in practical conductors by *tailoring the microstructure* of the superconductor and in the optimized case the  $J_C$  can be enhanced by one or two orders of magnitude in practical superconductors in technically useful magnetic fields.

In a practical superconductor, there will be a large number of flux lines interacting with each other and interacting with different pinning centers. The bulk flux pinning depends on the basic interactions between the individual flux lines (flux line-flux line) and between flux lines and individual pinning centers (flux line-pinning center). For a weak interaction between the flux lines (the magnetic interaction between flux lines is repulsive) the FLL acts as a two dimensional elastic crystalline solid. In this case there will be as many flux lines as possible are located on the pinning centers. If the number density of flux lines is less than or equal to the number of pinning centers (for instance in small applied fields) then each flux line is

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<sup>1</sup>To nucleate a flux line within the superconductor, the system must provide enough energy (This energy per unit length of flux line, called the condensation energy, is given by the volumetric free energy due to the magnetic field within the flux line) to convert the core of the flux line to the normal state. If the flux line is centered on a flux pinning center such as a void or normal conducting inclusion of radius  $\xi$ , the condensation energy needed to produce the normal core of the flux line would be saved, and the flux line would see a lower free energy at the location of the void than it would be in the bulk. That is, a pinned vortex has a lower free energy than a free vortex in a superconductor. The result of this free energy change is that the flux line requires an increase in its energy per unit length equal to the condensation energy, to move away from the flux pinning center. Thus, the flux pinning center holds the flux lines from moving and hence reduces the dissipation [page-97-102 of ref: 7].

individually pinned and the bulk pinning force is large. On the other extreme in which the interaction between the flux lines is strong, the FLL acts as a two dimensional rigid crystalline solid. In this case, the bulk pinning force due to a collection of randomly distributed pinning centers will be small over the completely rigid FLL. However, for practical polycrystalline systems the correct description of pinning lies somewhere between these two extremes of direct summation and rigid FLL lattice [page-97-102 of ref: 7].

### 1.3 Superconducting materials

Mercury (Hg) is the first material observed to be superconducting in 1911 by Kamerlingh Onnes. Now, nearly after one century of the discovery of the phenomena, thousands of materials including metals, alloys, binary and multicomponent compounds of metals, ceramics, doped fullerenes and organic molecules are found to be superconducting with transition temperatures ranging from a milli kelvin to  $\sim 150$  K [8–10]. Many materials, non-superconducting under normal conditions, become superconducting under pressure, upon irradiation or charge doping, and some materials in thin film form [11].

Table 1.1 gives some of the superconducting materials of various classes. Among the simple elemental superconductors Li has the highest  $T_C$  of 20 K under high pressure while Nb has the highest  $T_C$  of 9.25 K under normal conditions. Highly conducting ordinary metallic materials like Cu, Ag and Au are non-superconductors even to the lowest temperature studied. Al is superconducting and has a  $T_C$  of 1.18 K in bulk and 3.6 K in thin film form. Intermetallic materials with the A15 crystal structure such as  $\text{V}_3\text{Si}$ ,  $\text{Nb}_3\text{Sn}$ ,  $\text{Nb}_3\text{Ga}$  and  $\text{Nb}_3\text{Ge}$  have higher transition temperatures than the elemental superconductors. Of these A15 superconductors,  $\text{Nb}_3\text{Ge}$  has a  $T_C$  of 23.2 K and this was the highest  $T_C$  for a superconductor for many decades, before the mid 80's [chapter 3 page 59 of ref: 6]. All these simple elemental, alloy and intermetallic superconductors that have  $T_C$  at or below the  $\sim 23$  K are known as the low temperature superconductors (LTS) and are well explained by the BCS theory of superconductivity.

The discovery of superconductivity in copper oxide systems was a breakthrough in superconductivity research. In 1986 Bednorz and Müller reported the existence of superconductivity in  $\text{LaBaCuO}$ , at a surprisingly

Table 1.1: Superconducting materials under various classifications. Data for the table are taken from [6, 10–17]

Type/class	Example	$T_C$ (K)
Elements	Hg	4.2
	Nb	9.2
	Li (under pressure)	20
	B (under pressure)	11
	W (thin film)	5.5
	Pd (irradiated)	3.2
Amorphous materials	U <sub>85.7</sub> Fe <sub>14.3</sub>	1.0
	Th <sub>80</sub> Co <sub>20</sub>	3.8
Alloys	NbTi	9.0
	MoTc	16.0
A15 type (A <sub>3</sub> B)	Nb <sub>3</sub> Sn	18.0
	Nb <sub>3</sub> Ge	23.2
Laves phase (AB <sub>2</sub> )	ZrV <sub>2</sub>	9.6
	LaOs <sub>2</sub>	8.9
Chevrel phase (AB <sub>x</sub> Mo <sub>6</sub> l <sub>8</sub> )	PbMo <sub>6</sub> S <sub>8</sub>	12.6
	Sn <sub>1.2</sub> Mo <sub>6</sub> S <sub>8</sub>	14.2
Heavy electron systems	UPd <sub>2</sub> Al <sub>3</sub>	2.0
Organic materials	(TMTSF)PF <sub>6</sub> <sup>a</sup>	0.9
	(BEDT-TTF) <sub>2</sub> Cu[N(CN) <sub>2</sub> ]Br <sup>b</sup>	0.6
Magnetic material	ErRh <sub>4</sub> B <sub>4</sub>	10
Doped Fullerenes	Cs <sub>3</sub> C <sub>60</sub>	47.4
	Rb <sub>2.7</sub> Tl <sub>2.2</sub> C <sub>60</sub>	45
Borides	<b>MgB<sub>2</sub></b>	<b>39</b>
	ZrB <sub>12</sub>	5.82
	YRh <sub>4</sub> B <sub>4</sub>	11.3
Borocarbides	YPd <sub>2</sub> B <sub>2</sub> C	23
Oxides	Ba <sub>0.6</sub> K <sub>0.4</sub> BiO <sub>3</sub>	30
	LiTi <sub>2</sub> O <sub>4</sub>	13.7
Cuprates	YBa <sub>2</sub> Cu <sub>3</sub> O <sub>7</sub>	92
	Bi <sub>2</sub> Sr <sub>2</sub> Ca <sub>2</sub> Cu <sub>3</sub> O <sub>10</sub>	110
	Hg <sub>2</sub> Sr <sub>2</sub> Ca <sub>2</sub> Cu <sub>3</sub> O <sub>10</sub>	135
Oxypnictides	SmO <sub>0.9</sub> F <sub>0.1</sub> FeAs	55
	NdO <sub>0.82</sub> F <sub>0.18</sub> FeAs	51

<sup>a</sup> TMTSF = tetra-methyl-tetra-selenium-fulvalene<sup>b</sup> BEDT-TTF = bis-ethylene-dithia-tetra-thiafulvalene

high  $T_C$  of  $\sim 30$  K, [18], initiating the era of high  $T_C$  superconductivity (HTS). The discovery of superconductivity in the mixed YBaCuO compound system with  $T_C$  above 90 K higher than the boiling temperature of

liquid nitrogen (77 K) was another milestone in the search for new HTS materials [19, 20]. For years, copper oxide systems dominated the condensed matter field research and now a lot of HTS materials have been discovered, with  $T_C$  above 100 K.

The discovery of superconductivity in MgB<sub>2</sub>, a binary intermetallic with an unusually high  $T_C$  of 39 K by Jun Akimitsu's group [21] in Japan in 2001 surprised the condensed matter research field. Though the  $T_C$  of MgB<sub>2</sub> is much below the copper oxide based HTS, it generated a great deal of interest in both theoreticians and experimentalists worldwide. MgB<sub>2</sub> has the highest  $T_C$  among non-cuprate oxide bulk superconductors, under normal conditions. Recently Iron based layered compounds are found to be superconducting with  $T_C$  comparable and higher to that of MgB<sub>2</sub>.  $T_C$  values of above 50 K and  $H_{C2}$  values of the order of 100 T were reported for the Iron based superconductors [16, 17, 22]. However they contain the toxic arsenic and the fabrication into wires/tapes with better properties is not standardised yet. MgB<sub>2</sub> is free from most of the limitations of HTS and has a higher  $T_C$  than the presently using LTS materials.

## 1.4 Applications of superconductors

The unusual physical properties of superconductors resulted in some remarkable applications in specific areas. Superconducting materials can replace the conventional materials in many applications and with better performance. The choice between conventional and superconductive materials is generally related to technical and economical aspects, and the latter is the main factor limiting the widespread use of superconductors in practical applications. However, in many fields the superconducting technology is often the only possibility for achieving the required performance. By using superconducting components, the size and weight of instruments and devices can be reduced compared to conventional techniques which is an important issue for fields like space applications. Today superconductors have a wide range of commercial and industrial applications in energy production, storage, and its distribution, in sensor materials, in microwave communication systems and most importantly in high field magnets. The special issue of *Supercond. Sci. Technol.* published on 15 February 2006 discusses the status and future of some major applications of superconductivity in different countries. The main application sectors of superconducting materials are tabulated in table 1.2.

Table 1.2: General applications of superconductors

Area/Field	Applications
Energy/Power: Generation & Storage	Generators, SMES, Superconducting bearings for flywheel storage
Energy/Power: Distribution	Cables, Transformers, Current leads, FCLs, Motors.
Magnets	NMR, MRI instruments, Magnetic confinement of plasma in Fusion reactors, Particle accelerators, High field magnets.
Electronics	In microwave filters, Digital logic circuits as RSFQ, Sensor applications
Biomedical	Detection of extremely small neuromagnetic fields, Magnetoencephalography (MEG), Magnetocardiography (MCG)
Industrial	Magnets for shielding and separation, sensors
R & D	Superconducting RF cavities in particle accelerators, Synchrotrons and High field magnets.
Other applications	Magnetic levitation, Magnetohydrodynamics, Space applications

Superconducting magnets have exclusive uses in some commercially available instruments like MRI instruments in medical field, and for high field magnets for NMR and particle accelerators. NbTi is the mostly used superconducting material for MRI magnets. For high field magnets, Nb<sub>3</sub>Sn is mostly used and some HTS based inserts are also developed for still higher fields. HTS based magnets inserted in high field LTS magnets are tested upto  $\sim 25$  T [23]. Superconducting solenoids are being used for bending and focusing of high energy particles in high-energy particle physics labs like BNL, CERN, DESY and the Fermi Laboratory. Besides solenoids, superconducting RF cavities are also find applications in particle accelerators. Large-scale application of superconducting cavities to electron and ion accelerators is established at many laboratories around the world [24]. With the development of cryocoolers, various kinds of cryogen free superconducting magnets with fields of the order of 20 T are now developed for practical applications [25, 26]. In fusion reactors, the plasma temperature needed for energy production is several million degrees, and high field superconducting magnets are required to confine the plasma. The International Thermonuclear Experimental Reactor (ITER) project is engaged in the development of fusion reactor and a large quantity of LTS superconductors is being manufactured for the project [27, 28].

Since the supercurrent in a superconductor persists for a very long time, superconductors have applications in energy storage also. Superconducting Magnetic Energy Storage (SMES) can store mega joules of energy, without resistive losses. SMES systems capable of storing mega joules of energy has been tested and installed in various places. They are receiving more importance with regard to future electrical power grids. Details of a 3MJ/750 kVA SMES system developed by the Korea Electrotechnology Research Institute (KERI) can be found in [29].

One of the peculiar properties of superconductivity is that they find applications in extremely weak and extremely high magnetic fields. Superconducting magnets provides high fields while superconducting thin films are used for the detection of extremely weak fields. The Superconducting Quantum Interference Device (SQUID) based on the Josephson effect is the most sensitive magnetometer. SQUID based technology is widely used for the non-invasive clinical measurements of weak bio-magnetic fields: especially in the mapping of extremely weak magnetic signals from the human brain. In material science and physics research SQUID based magnetometers are being used for magnetic characterization of materials. The Magnetic Property Measurement System (MPMS) and Physical Property Measurement System (PPMS) are two well-known commercial instruments based on superconductor technology.

Superconducting cables can replace the conventional copper/aluminium based cables in electric power transmissions. Cost of the superconducting technology compared to the conventional is the main hurdle in the limited use of superconductors in this sector. Conductors made of BSCCO-2223 are being applied in variety of power transmission cables and distribution cables [30]. The world's first high temperature superconductor power transmission cable system in a commercial power grid system was energized recently in New York, USA.<sup>1</sup> Another major application of superconductors in electric power grid is for the control of fault currents in electrical transmission and distribution networks, as Superconducting Fault Current Limiters (SFCL). Fault Current Limiters (FCL) restrict the maximum current through a network and protect the devices from an accidental over current. Several groups are actively involved in developing SFCL for industrial applications. A 1.2 MVA 10.5 KV Bi2212 LN<sub>2</sub> cooled SFCL

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<sup>1</sup>The 138 kV, ~ 609 m cable system is the longest superconducting system in the world energized on 22 April 2008. Information is from [www.ams.com/pdf/HTSC\\_AN\\_0109\\_A4\\_FINAL.pdf](http://www.ams.com/pdf/HTSC_AN_0109_A4_FINAL.pdf)

has been developed and commissioned for protecting a hydroelectric plant auxiliary transformer circuit [page 547 of ref: 7].

Superconducting thin films are finding more applications in electronic industry. Rapid Single Flux Quantum (RSFQ) is an emerging digital electronics technology that relies on quantum effects in superconducting materials to switch signals, instead of transistors. The quantum pulses are switched by Josephson junctions. Superconducting components such as resonators, filters and delay lines with performance far superior to conventional technology are being widely used in microwave electronics. HTS microwave technology is a promising one, especially at frequencies below 3Hz. Another important application of superconductors is magnetic levitation in transportation (eg: Maglev trains). For maglev systems YBCO is preferred, since it exhibits high magnetic irreversibility field at LN<sub>2</sub> temperatures and has the ability to grow into large grains. Due to the expulsion of magnetic field in the superconducting state, a superconductor can be used for magnetic shielding applications.

Among the various applications described above MgB<sub>2</sub> has the potential of replacing existing superconductors in many fields with improved performance and/or low cost. The possible applications of MgB<sub>2</sub> conductors include magnets for MRI, fusion reactors, high energy particle accelerators, and for future high field magnets. Other possible applications of MgB<sub>2</sub> includes superconducting transformers, motors, generators, SMES and particularly in SFCLs. Besides the conductor applications MgB<sub>2</sub> thin films/junctions can find a place in future electronics also.

## 1.5 Relevance of MgB<sub>2</sub>

As discussed in the previous section superconductors have important practical applications in many fields. The present and future applications have two potential market for superconducting wires: high field magnet applications (such as NMR, MRI magnets, magnets for particle accelerators and plasma confinement in fusion reactors) and electrical power sector (applications such as transmission cables, SMES, transformers, FCLs, motors, generators).

Though thousands of materials are found to be superconducting, only a handful of them are useful for practical applications. Table 1.3 compares

Table 1.3: Properties of MgB<sub>2</sub> and other practical superconductors. Order of  $J_C$  values are at 4.2 K, in self-field.  $H_{C2}$  values are at 4.2 K. Data are taken from [16, 31–38]

Material	$T_C$ (K)	Anisotropy	$J_C$ (A/cm <sup>2</sup> )	$H_{C2}$ (T)	$\xi(0)$ (nm)	$\rho(\text{at } T_C)$ $\mu\Omega\text{cm}$
NbTi	9	Negligible	$10^6$	11-12	4-5	60
Nb <sub>3</sub> Sn	18	Negligible	$10^6$	25-29	3	5
Nb <sub>3</sub> Al	20	Negligible	$10^6$	30-45	4-5	10-60
MgB <sub>2</sub>	39	1.5-5	$10^6$	30-40	5-12	0.4
FeAs based	25-56	8-15	$10^5$	25-100	2-10	200-10 <sup>4</sup>
Bi2223	110	50-200	$10^7$	>100	1.5	40-60
YBCO	92	5-7	$10^6$	>100	1.5	150-800

some of these superconducting materials with MgB<sub>2</sub>. The most widely used commercial superconductors are NbTi and Nb<sub>3</sub>Sn, two LTS materials. NbTi, having a  $T_C$  of 9 K and  $H_{C2}$  (4.2 K)  $\sim$  10-12 T, has high strength and ductility and is easy to fabricate into long wires. NbTi occupies most of the low field magnets in commercial MRI instruments. The high energy physics (HEP) community and the MRI industry are the main consumers of NbTi over the years. The use of NbTi is limited to fields < 10 T and the operation of NbTi needs liquid helium temperatures, which makes its use costly. Nb<sub>3</sub>Sn has a  $T_C$  of  $\sim$  18 K and  $H_{C2}$  (4.2 K) of more than 20 T and is used in low temperature high field magnets. Though it offers much higher fields and operating temperature compared to NbTi, it is brittle, quite sensitive to strains and difficult to fabricate, and hence more costly than the NbTi. Both NbTi and Nb<sub>3</sub>Sn had undergone many years of research and are commercially available. Another A15 material Nb<sub>3</sub>Al with much higher field capacity and strain tolerance than the Nb<sub>3</sub>Sn is considered for conductor development. Nb<sub>3</sub>Al has a  $T_C$  of 20 K and  $H_{C2}$  of 40 T at 4.2 K. However the manufacturing of Nb<sub>3</sub>Al conductor with good properties is extremely difficult and it will take few more years to enter into the commercial market. The nearly discovered FeAs based materials show superconductivity with  $T_C$  26-55 K and  $H_{C2}$  values 20-100 T, however the preparation of quality wires/tapes based on these materials is extremely difficult.

Most of the HTS materials have  $T_C$  above 77 K and higher  $H_{C2}$  values than the LTS. But the HTS conductors faced many technical problems in making wires and coils. Their conductor fabrication is not so easy as compared to the LTS materials and needs costly Ag as sheath material and



the field performance at higher temperatures is not promising. The most important and commercially interesting HTS are BSCCO (Bi-2223 and Bi-2212) and YBCO (Y123). Bi-2223 has a  $T_C$  of 110 K, Bi-2212 has a  $T_C$  of  $\sim 85$  K, and the  $T_C$  of YBCO is  $\sim 92$  K. The  $H_{C2}$  of all the three HTS is more than 100 T at 4.2 K. BSCCO conductors are fabricated in tape geometry using the Powder-In-Tube (PIT) method. Ag sheathed BSCCO conductors known as the first generation HTS conductors are being commercially produced by a number of companies like American Superconductors, Sumitomo Electric Industries Ltd etc. Coated conductor technique is most suitable for YBCO. YBCO based coated conductor is considered as the second generation HTS conductors. HTS have high anisotropy and hence the current carrying capacity is low in untextured conductors. Due to their high anisotropy, for practical applications, for BSCCO uniaxial and for YBCO biaxial texturing is preferred. The HTS materials also have weakly connected grain boundaries so that the intergrain connectivity is also a big problem. For YBCO conductors grain orientation is also important.

MgB<sub>2</sub> has a higher  $T_C$  of 39 K as compared to the conventional LTS and is free from most of the limitations of HTS. Thus comparing with currently using LTS, NbTi and Nb<sub>3</sub>Sn, MgB<sub>2</sub> has the advantage of higher  $T_C$  and  $H_{C2}$ . Compared to most of the HTS MgB<sub>2</sub> has a  $T_C$  two to three times lower. The main advantage of MgB<sub>2</sub> compared to HTS is that in the bulk polycrystalline form it exhibits a critical current density three orders of magnitude higher than polycrystalline HTS. MgB<sub>2</sub> has weak link free grain boundaries and the grain boundaries act as strong flux pinners. Doped MgB<sub>2</sub> wires have already reached  $H_{C2}$  values as high as 33 T, higher than that of Nb<sub>3</sub>Sn and a record high value of 55 T in coated fibers [39]. Figure 1.4 shows a comparison of H-T phase diagram of typical MgB<sub>2</sub> with the NbTi and Nb<sub>3</sub>Sn. Primitive Powder-In-Tube conductors of MgB<sub>2</sub> could attain nearly  $10^6$  A/cm<sup>2</sup> critical current densities in self field at 4.2 K. Experiments on thin films suggest more than 10 times higher  $J_C$  values for wires or tapes with smaller grain size, full density, and perhaps with suitable additives. MgB<sub>2</sub> based magnets are already tested for low field applications and MgB<sub>2</sub> seems to be the most promising material for next generation high field magnets and a strong competitor for Nb<sub>3</sub>Sn and NbTi.

Good quality MgB<sub>2</sub> conductors with high critical current density can be prepared with heat treatment of PIT *in situ* wires/tapes at 600-800 °C for 5-30 minutes. This is really an advantage from an industrial point of view since many of the HTS and LTS need much higher temperatures and/or

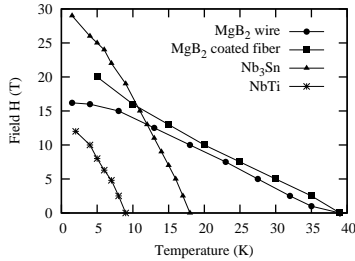


Figure 1.4: Comparison of H-T phase diagram of typical  $\text{MgB}_2$  and the LTS.

urations for manufacturing. The density of  $\text{MgB}_2$  is  $2.6 \text{ g/cm}^3$ , much lower than other superconductors and ordinary copper. This makes  $\text{MgB}_2$  suitable for specific light-weight applications, such as space application. Both Mg and B, the reactants of  $\text{MgB}_2$  and the sheath materials used are inexpensive. Thus  $\text{MgB}_2$  is economical for practical applications and the cost/performance ratio for  $\text{MgB}_2$  is much lower than other superconductors [40, 41].

$\text{MgB}_2$  is most suited for applications around 20-25 K where cryocoolers can be used for cooling. Several manufacturers have already fabricated stabilized  $\text{MgB}_2$  conductors in kilometers of length both by *ex situ* and *in situ* method, for various applications (review articles [42–44]). Industrial scale production of  $\text{MgB}_2$  conductors has started by manufacturer Hyper Tech Research Inc., Columbus, Ohio and Columbus Superconductors, Genova, Italy. One of the major applications of  $\text{MgB}_2$  in the near future is for MRI magnets. MRI instruments based on  $\text{MgB}_2$  operating at 20-25 K using cryogen free cryocoolers will be more economical than the conventional NbTi based MRI instruments. Laboratory scale as well as demonstration level  $\text{MgB}_2$  based MRI systems with high performance and low price are developed in many countries [45]. Based on the use of  $\text{MgB}_2$  conductors supplied from Columbus superconductors, ASG superconductors together with Paramed Medical Systems recently constructed an open MRI system [46].

$\text{MgB}_2$  has also applications as current leads and fault current limiters in specific areas. The first application of  $\text{MgB}_2$  conductors as current leads was realized on the Japanese satellite ‘Suzaku’ which was launched in July 10, 2005 in Japan. Ultra thin  $\text{MgB}_2$  conductors with diameters down to

50  $\mu\text{m}$  have been developed for the current lead and liquid hydrogen level sensor applications [47]. With operational advantages at intermediate temperature (20-30 K) and low cost, MgB<sub>2</sub> is very attractive as a cost effective FCL. Work has been reported on the current limiting properties of MgB<sub>2</sub> wires at 50 Hz in the 20-30 K range [48, 49]. MgB<sub>2</sub> based FCL can be a strong competitor for the inductive FCL coils using HTS conductors. MgB<sub>2</sub> based thin films and tunnel junctions are being fabricated with reasonably good properties for applications in electronics and allied areas. For RSFQ applications, a reliable MgB<sub>2</sub> technology could boost superconducting electronic applications. The two band gap nature of MgB<sub>2</sub> can also be exploited for novel applications [50].

*In a nutshell MgB<sub>2</sub> is quicker (formation), cheaper (cost/performance) and better (for specific applications) compared to many of the practical superconductors.*

## 1.6 Properties of MgB<sub>2</sub> superconductor

Magnesium diboride (MgB<sub>2</sub>) is a binary intermetallic compound with a simple hexagonal crystal structure (AlB<sub>2</sub> type structure). It is a brownish-black material, known since early 1950's to the materials science community and is even commercially available. In 1953 Jones and Marsh [51] and Russell *et al* [52] reported the formation of MgB<sub>2</sub> phase with the interaction of Mg and amorphous B in hydrogen and/or argon atmospheres. For the Mg–B system, besides the MgB<sub>2</sub> phase, many observed/proposed formation of other magnesium boride phases such as MgB<sub>4</sub>, MgB<sub>6</sub>, MgB<sub>7</sub>, MgB<sub>12</sub>, MgB<sub>20</sub> etc [52–57]. Now, formation of the four phases MgB<sub>2</sub>, MgB<sub>4</sub>, MgB<sub>7</sub> and MgB<sub>20</sub> are well established [55–57].

### 1.6.1 Crystal structure of MgB<sub>2</sub>

MgB<sub>2</sub> has hexagonal crystal structure (figure 1.5) with space group  $p6/mmm$  [12], which is common among diborides. The boron atoms form graphite like honeycomb network and the Mg atoms are located at the pores of these hexagons. In the unit cell the atomic positions are (0,0,0) for Mg (Weizkoff symbol 1a) and  $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$  and  $(\frac{2}{3}, \frac{1}{3}, \frac{1}{2})$  for B (Weizkoff symbol 2d) atoms [58, 59]. The coordination polyhedra are (B<sub>12</sub>Mg<sub>8</sub>) for Mg and (Mg<sub>6</sub>B<sub>3</sub>) for B. The lattice parameters are  $a = 3.084 \text{ \AA}$  and  $c = 3.524 \text{ \AA}$  and the inter atomic distances are: B-B intralayer 1.780  $\text{\AA}$ , Mg-Mg intralayer 3.084  $\text{\AA}$ ,

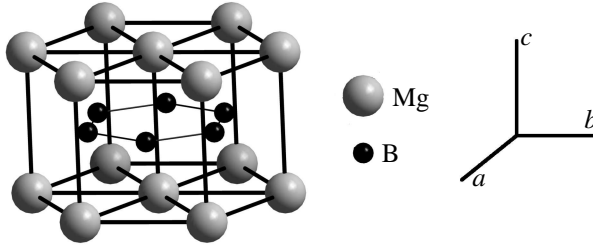


Figure 1.5: Crystal structure of  $\text{MgB}_2$ .

$\text{Mg-Mg}$  interlayer  $3.524 \text{ \AA}$  and  $\text{Mg-B}$   $2.5 \text{ \AA}$  [12, 59]. The in-plane B-B distance is almost half that of the inter-plane B-B distance.

## 1.6.2 Physical and superconducting properties of $\text{MgB}_2$

$\text{MgB}_2$  is a brittle material like the HTS materials. Typical polycrystalline  $\text{MgB}_2$  has a grain size of  $10 \text{ nm}$ - $10 \text{ }\mu\text{m}$  [60–64]. The anisotropy of  $\text{MgB}_2$  is  $1.5$ - $5$  [32–34] and is low compared to the highly anisotropic HTS. This low anisotropy means there is no need of texturing as in the case of HTS for making wires with high  $J_{\text{CS}}$ . The coherence length of  $\text{MgB}_2$  is  $\sim 5$ - $12 \text{ nm}$  and the penetration depth is  $100$ - $140 \text{ nm}$  with a GL factor of  $K \sim 26$  [35] at absolute zero. Due to the large coherence length, higher than the inter atomic spacing, the weak link problem is not severe in  $\text{MgB}_2$ .  $\text{MgB}_2$  has two superconducting gaps in the superconducting state,  $\Delta_1 \sim 5$ - $7 \text{ meV}$  and  $\Delta_2 \sim 1.5$ - $2.0 \text{ meV}$  [65, 66].

$\text{MgB}_2$  has a very sharp  $T_{\text{C}}$  around  $39 \text{ K}$  [12, 66] and has a very narrow transition width of less than  $1 \text{ K}$ . The  $T_{\text{C}}$  of  $\text{MgB}_2$  is nearly double that of  $\text{Nb}_3\text{Sn}$  and nearly four times that of  $\text{NbTi}$  but still much lower than the liquid nitrogen temperature. The isotopic  $\text{B}^{10}$  substitution slightly increases the  $T_{\text{C}}$  to  $40.25 \text{ K}$  [67]. The research for enhancing the  $T_{\text{C}}$  by substitutions of aliovalent and isovalent atoms with different radii hasn't given satisfactory results as expected. Most of the substitutions resulted in a decrease of  $T_{\text{C}}$ . The substitution of Al to the Mg site and C to the B site reduced the  $T_{\text{C}}$  and the superconductivity is lost for higher doping [68–70]. The substitution of Al caused a structural transition at higher levels [68]. The normal state of  $\text{MgB}_2$  is metallic and the normal state resistivity is much lower than that of other superconductors. For clean  $\text{MgB}_2$  samples a very low

normal state resistivity  $\rho(T_C)$  of  $0.4 \mu\Omega\text{cm}$  and a high Residual Resistivity Ratio (RRR) of  $\sim 20$  are observed [71].

MgB<sub>2</sub> is a type II superconductor and is well within the clean limit of superconductivity. The depairing current density is  $\sim 10^7 \text{ A/cm}^2$  [72], one order of magnitude lower than that of the HTS materials. The observed transport critical current densities are of the order of  $10^6 \text{ A/cm}^2$  at 4.2 K in self field,  $\sim 3.8 \times 10^4 \text{ A/cm}^2$  in 6 T and  $10^4 \text{ A/cm}^2$  in 8 T [73]. The transport  $J_C$  is of the order of  $10^4 \text{ A/cm}^2$  at 30 K in 1 T field [74]. For Cu stabilized multifilamentary conductors a transport  $J_C$  of  $1.75 \times 10^5 \text{ A/cm}^2$  was measured at 5 T, 4.2 K [75]. The intergranular  $J_C$  of MgB<sub>2</sub> is also high compared to HTS materials. Pure MgB<sub>2</sub> has low lower critical field  $H_{C1}(0)$  of less than 50 mT [76, 77], upper critical field  $H_{C2}$  of 15-20 T and irreversibility field 6-12 T [35, 71, 76, 78] at 4.2 K. Doped conductors have high  $H_{C2}$  and the maximum  $H_{C2}$  observed for SiC added MgB<sub>2</sub> wires is 33 T, much higher than that of the Nb<sub>3</sub>Sn [79].

### 1.6.3 Advantages of two gap superconductivity

MgB<sub>2</sub> is the first superconductor which showed two distinct energy gaps in the superconducting state. The two energy bands arise from the  $\sigma$  (formed from the  $sp^2$  hybrids of boron  $2s$  and  $p_{x,y}$  orbitals) and  $\pi$  (originated from the boron  $p_z$  orbital) bands. For a detailed description of the origin of superconductivity and the energy bands please see the review article [80]. From an application point of view the two gap nature is significant and a detailed discussion on this is presented in [81]. For the single band LTS increase in  $H_{C2}(0)$  is expected by the introduction of charge-carrier scattering impurities into the lattice structure. The charge scattering causes decrease in coherence length and increase in the  $H_{C2}$  values. This rule is used for the design and manufacturing of LTS materials over the years. Being a two band superconductor, MgB<sub>2</sub> has three scattering channels with different scattering rates: the intra-band scattering within the  $\sigma$  and  $\pi$  bands and the inter-band scattering between the  $\sigma$  and  $\pi$  bands. Tuning of these inter and intra band scattering rates make it possible to achieve high  $H_{C2}$  values in MgB<sub>2</sub>, much beyond to the reach of NbTi and Nb<sub>3</sub>Sn. Some best MgB<sub>2</sub> polycrystals have shown  $H_{C2}$  of 40-50 T and highest  $H_{C2}$  of  $\sim 74 \text{ T}$  was reported for a thin film [82].

## 1.7 Critical Issues (major challenges) of MgB<sub>2</sub>

For commercial applications of MgB<sub>2</sub> multifilamentary conductors with large number of fine filaments having high  $H_{C2}$  and  $J_C(T, H)$  values must be produced in long lengths at a low cost. The fabrication of long length MgB<sub>2</sub> wires is relatively easy and more economical. However there are many critical issues, which are to be addressed seriously. These include the fabrication of good quality long length conductors or cables at a reduced cost and the improvement in the performance of the conductors.

### 1.7.1 Issues regarding fabrication

Phase purity and homogeneity of the superconductor are important factors, which need some attention in the fabrication of long length conductors. Since Mg is highly volatile and has strong affinity to oxygen in the *in situ* fabrication, Mg loss and MgO formation are the main causes for the inhomogeneities and impurities. Mg loss can cause non-stoichiometry and the formation of higher borides (like MgB<sub>4</sub> or MgB<sub>7</sub>) as impurities. Formation of MgO and other impurities limits the active current carrying area and weaken the grain connectivity and hence reduces the critical current density [12, 83, 84]. Many prefer synthesis in excess Mg environment and inert/vacuum atmosphere to compensate the Mg loss and oxidation.

The wide difference in melting points of Mg (650 °C) and B (2080 °C) doesn't favor solid-solid or liquid-liquid reactions. The sinterability of MgB<sub>2</sub> grains are poor also. The *in situ* samples formed by the liquid-solid reaction of Mg and B are highly porous and have low density compared to the theoretical density of MgB<sub>2</sub>. This is mainly due to the voids remaining from the prior Mg particles during the MgB<sub>2</sub> formation ( $V_{Mg} + V_{2B} > V_{MgB_2}$ ) [84]. The high porosity also limits the grain connectivity and hence the intergrain current transport [84]. More research and new techniques are needed to decrease the porosity and to increase the density of the samples.

Another problem with the fabrication is the reactivity of Mg with most of the commonly used sheath materials. The reacted secondary phases at the sheath core interface act as barrier for the current transfer from the outer sheath to the superconducting core and also restricts the local heat developed to flow out to the sheath, during a possible quenching. Barrier materials such as Nb or Ta can reduce the reaction between the core and sheath, but both Nb and Ta are expensive. Another major obstacle for

practical MgB<sub>2</sub> conductors is the insufficient thermal stabilization, leading to quenching of the conductor in high currents. Conductive Cu gives better thermal stabilization for LTS materials and Ag for Bi based conductors. For MgB<sub>2</sub> also Cu sheath with Nb or Ta barrier and SS or Fe reinforcement can have good thermal stabilization and mechanical strength.

### 1.7.2 Issues regarding property improvement

Though MgB<sub>2</sub> has high self field  $J_C$  comparable to NbTi and Nb<sub>3</sub>Sn at low temperatures, the  $J_C$  falls rapidly with field and temperature, due to poor vortex pinning, and low irreversibility field. Since MgB<sub>2</sub> has a rigid lattice with two simple elements in the structure, the density of defects produced during synthesis is too low to provide sufficient flux pinning at higher fields. Only grain boundaries are effective pinning centers in pure MgB<sub>2</sub>, thus MgB<sub>2</sub> samples with fine grains are needed for better properties. The irreversibility field of MgB<sub>2</sub> is only half of its upper critical field ( $H_{irr} \sim 0.5 \times H_{C2}$ ), whereas for NbTi and Nb<sub>3</sub>Sn the irreversibility field is close to their respective upper critical fields ( $H_{irr} \sim 0.8 \times H_{C2}$ ). The low irreversibility field and poor flux pinning cause rapid decrease in  $J_C$  at high fields. This limits the temperature and field range where MgB<sub>2</sub> could be superior to Nb<sub>3</sub>Sn to above 10 K and 2-3 T. In order to compete with the Nb<sub>3</sub>Sn for liquid helium temperature applications, the  $J_C(H)$  of MgB<sub>2</sub> must be improved. This can be achieved by improving the flux pinning at high fields, increasing the  $H_{irr}$  and decreasing the electromagnetic anisotropy etc [84–86].

## 1.8 Synthesis of MgB<sub>2</sub> superconductor

During the last 8-9 years, various fabrication/preparation methods are used to synthesis MgB<sub>2</sub> based superconductors in bulk, powder, thin film, wire, tape as well as single crystal forms. Since the present work focuses on bulk and wires/tapes the details of which only are discussed. MgB<sub>2</sub> based superconductors are prepared either by sintering of commercially available MgB<sub>2</sub> powder or from elemental Mg and B powders. Preparation of MgB<sub>2</sub> based superconductors using commercial/as-prepared MgB<sub>2</sub> is known as *ex situ* while from Mg and B powders/sources is known as *in situ* method. Both *ex situ* and *in situ* have their merits and demerits.

In the *ex situ* method the commercial MgB<sub>2</sub> powder is pelletized and heat treated at elevated temperatures of 800-1200 °C for 1-5 hours in vacuum or inert atmosphere. The final properties of *ex situ* samples depends on the quality of commercially available powder. The *ex situ* MgB<sub>2</sub> has better homogeneity and higher density than the *in situ* one. However for better superconducting properties the *ex situ* samples need much higher sintering temperatures and the doping of other elements is restricted compared to the *in situ* samples. The *in situ* method produces MgB<sub>2</sub> with low density, but has the advantage of easy tailoring by chemical addition/doping for better superconducting properties.

### 1.8.1 Bulk samples

Several synthesis procedures are reported for the preparation of *in situ* MgB<sub>2</sub> bulks with relatively low temperature and short durations of heat treatments [87–94]. The starting materials are Mg in powder/flakes/chips and amorphous/crystalline B in powder forms. Some groups use MgH<sub>2</sub> powder as Mg source [87, 88]. For the *in situ* preparation the starting materials (either pellet or powder mixture) are enclosed in Nb/Ta/Fe/SS/Quartz tubes/foils/ampoules and heat treated at 650-1000°C for 30 min-5 hours in vacuum or hydrogen/argon atmospheres. Considering the oxidation and vapor loss of Mg many prefer excess Mg environments also. Suitable sintering aids or mechanical alloying/ high energy milling are found to enhance the formation of MgB<sub>2</sub> phase at relatively lower temperatures with improved superconducting properties [89–92].

High energy ball milling allows reduction of particle size and more homogeneous mixing of the ingredients. Many groups now use this technique for the preparation of doped and undoped MgB<sub>2</sub> bulk samples, with fine grains and hence better superconducting properties. Contamination from the bowl, ball and milling media and particle agglomeration are two main hurdles of this method, and the performance of mechanically alloyed or high energy ball milled samples depends on various factors like nature and size of the ball and bowl, ball to powder ratio, speed and milling duration and the milling medium [91, 92].

Most of the *in situ* samples prepared by these methods have high porosity and very low density (only 50% of theoretical density in many cases). Methods like high pressure sintering (HPS) [76, 95, 96], hot isostatic pressing (HIP) [97, 98] and double step sintering (2-stage sintering) [99, 100]



are used to get highly dense MgB<sub>2</sub> bulk samples. Both high pressure sintering and hot isostatic pressing use high pressure for the densification and reduction of porosity. In these methods the precursor is subjected to high pressures of 0.5-5 GPa during the high temperature heat treatment at 700-1000 °C. The reported properties after HPS or HIP synthesis show some scatter with respect to the pressing system. The main advantage of this technique is the possibility of producing extremely high dense MgB<sub>2</sub> samples: even density close to 100% were prepared for an *ex situ* sample by this method. The main disadvantage is the sophisticated and costly instruments, which also limit the sample dimensions used for the method. Though the method is most suitable for bulk samples, some groups used it for small length wire/tapes with limited success. The reactive liquid Mg infiltration technique introduced by EDISON SpA (Italy) can produce bulk MgB<sub>2</sub> samples of different shape with higher densities. The method involves the reaction of liquid Mg with the B powders in a closed metallic container [101].

### 1.8.2 Wire and Tape samples

Over 50 years of conductor fabrication in LTS and 20 years of experience in HTS, helped researchers, to fabricate MgB<sub>2</sub> conductors of long length soon after the announcement of superconductivity in the material. Some of the fabrication techniques used for LTS and HTS can be applied to MgB<sub>2</sub> also. Diffusion of Mg into B fibers or wires, coating technique and Powder-In-Tube (PIT) method are employed for the fabrication of MgB<sub>2</sub> based conductors. Of these, PIT is the most popular and industrially preferred method.

#### Diffusion method

Mg diffusion into B wires is a relatively easy method by which commercially available B fibers or wires can be converted into superconducting MgB<sub>2</sub> wires. The first superconducting MgB<sub>2</sub> wires were prepared by this method [71]. Cunningham *et al* [102] also prepared MgB<sub>2</sub> wires by diffusing Mg into tungsten cored B fibers. By infiltrating a preform of B fibers with liquid Mg and subsequent reaction at elevated temperatures DeFouw *et al* [103] fabricated composite MgB<sub>2</sub> wires of several hundred continuous fibers within an Mg matrix. The phase homogeneity of the conductors produced by diffusion is poor and the method is suitable for short samples and the feasibility of making long length conductors needs to be studied.

## Coating techniques

Coated conductor technique is a well known process, widely used for the fabrication of commercially available YBCO conductors. For MgB<sub>2</sub> high  $H_{C2}$  and  $J_C$  values in applied fields are observed in thin films [12, 104] and so coated conductor technique is being tried in some labs. K. Komori *et al* [105] used sputtering technique to make MgB<sub>2</sub> coated conductor in hastelloy substrate with Ytria Stabilized Zirconia (YSZ) as buffer layer. The carbon alloyed MgB<sub>2</sub> coated conductor fabricated by Hybrid-Physical-Chemical Vapour Deposition (HPCVD) on SiC fibers with tungsten core by Ferrando *et al* showed a high  $H_{C2}$  of 55 T and high irreversibility field of 40 T at 1.5 K [39]. Using a new processing technique called the Molten Salts Electro Plating (MSEP) MgB<sub>2</sub> can be coated to stainless steel (SS) [106] substrate which gives higher chemical stability, higher plasticity and higher heat conductance than the widely used ceramic substrates. Even though the superconducting properties of coated conductors are normally superior to conductors fabricated by other techniques, the scaling up of this technique is not straight forward compared to the widely used PIT process.

## Powder-in-tube (PIT) method

Powder-in-tube method is the most popular method for achieving good quality wires of HTS Bi-2212 and Bi-2223. In PIT the precursor powder is filled in various metal tubes or sheaths [43, 44, 47, 60, 107–113]. The filling can be in air [107] or in an inert atmosphere [108]. These tubes are then mechanically rolled/extruded/drawn into desired size and shape followed by heat treatment. Heat treatment is usually done in vacuum or oxygen protective atmosphere. Intermediate annealing relieves the stress developed during drawing or rolling. In the case of MgB<sub>2</sub> the metallic sheath chosen must be chemically compatible with the MgB<sub>2</sub> and should not degrade the superconductivity.

PIT techniques can be used for fabricating multifilamentary conductors, which withstand larger uniaxial and bend strains than single filaments and exhibit a higher thermal stability. Hyper Tech Research developed a modified PIT process for low cost continuous production of MgB<sub>2</sub> wires [42, 43]. In the method, known as continuous tube forming/filling (CTFF) process, the precursor powder is dispersed on to a strip of metal as it is being continuously formed into a tube. The filled overlap closed tube is then inserted into hard metallic tubes as in PIT and drawn into the desired dimensions, followed by appropriate heat treatments.

PIT method is the most preferred for manufacturing long length multifilamentary MgB<sub>2</sub> conductors. Long length conductors in wire geometries (circular, square or rectangular cross sections), with filaments upto 61 have been fabricated. Some solenoid and racetrack coils are also demonstrated using PIT MgB<sub>2</sub> conductors. Hyper Tech Research Inc. and Columbus Superconductors are producing multifilamentary stabilized MgB<sub>2</sub> conductors with different geometries and sheath combinations. The critical current density for good quality wires/tapes is 10<sup>6</sup> A/cm<sup>2</sup> at self-field and 10<sup>4</sup> A/cm<sup>2</sup> at 10 T, both at 4.2 K. At 20 K and self field the typical samples have a  $J_C$  of 10<sup>5</sup> A/cm<sup>2</sup> [42–44].

## 1.9 Improvement of Flux pinning and in-field critical current density in MgB<sub>2</sub>

In the mixed state (vortex state) a superconductor is filled with quantized vortices (fluxons). In isotropic superconductors such as NbTi and Nb<sub>3</sub>Sn the vortex lines are continuous and no decoupling occurs. But in HTS compounds at high temperatures and fields the 3D vortex lines melts into 2D pancake vortices [114] which are weakly coupled, whose circulating screening currents are mostly confined within the superconducting CuO<sub>2</sub> planes. In the case of MgB<sub>2</sub> the vortices are line like similar to that of LTS and there is no such decoupling of the vortex lines. As discussed earlier, in applied fields the fluxons tend to move during transport current flow through the superconductor. The movement of fluxons causes a drastic decrease in the  $J_C$  in applied fields. In order to sustain high  $J_C$  values in applied fields, the movement of fluxons must be stopped. ie. the flux lines must be pinned.

Pinning centers in conventional methods of fabrication of low  $T_C$  superconductors are developed by modifying the thermomechanical processing. Finely dispersed nanosized nonsuperconducting  $\alpha$ -Ti phase precipitated during heat treatment is strong flux pinners in NbTi [115, 116]. For effective pinning the typical thickness of the  $\alpha$ -Ti phase must be 1-4 nm with a separation of 5-20 nm. In the case of Nb<sub>3</sub>Sn, grain boundaries are the dominant pinning centers [117]. The  $J_C$  of Nb<sub>3</sub>Sn is observed to be inversely proportional to the grain size [117] at low fields. Synthesis of Nb<sub>3</sub>Sn at low temperatures helps the formation of Nb<sub>3</sub>Sn phase with fine grain sizes, increases number of grain boundaries and  $J_C$  at high fields. In HTS materials grain boundaries, growth dislocations, crystal structural non uniformities,

impurity phases, precipitates, oxygen vacancies and other microstructural defects can act as effective pinning centers [118–120]. The introduction of secondary phases or normal impurities to the superconducting matrix improves the flux pinning property of HTS materials [121].

Grain boundary pinning, like in Nb<sub>3</sub>Sn is the dominating pinning mechanism in MgB<sub>2</sub> [61, 122–124] and the pinning improves with reduced grain size [125]. In MgB<sub>2</sub>, since lattice structure is rather rigid and the number of elements in the structure is only two, the density of defects introduced by preparation procedures is too low to provide effective flux pinning. Pinning in pure MgB<sub>2</sub> is mainly provided by grain boundaries. It is found that in MgB<sub>2</sub> the aperiodic semicrystalline defects trapped in the crystalline phase act as intense vortex pinning centers and significantly enhance the high field performance of MgB<sub>2</sub> [126]. Inclusions and doping can improve the flux pinning of MgB<sub>2</sub> strongly.

Irradiation of high energy radiation introduces artificial defects (point or extended) in a crystal. In the case of MgB<sub>2</sub> superconductor this type of intentionally introduced defects can act as strong flux pinners and also scattering centers: both improve the in-field  $J_C$  as well as the  $H_{C2}$ . Bugoslavsky *et al* [127] improved the high field  $J_C$  of MgB<sub>2</sub> by producing atomic scale defects by proton irradiation. Similar results of highly enhanced  $J_C$  and  $H_{C2}$  were observed for neutron irradiated samples [128, 129]. Though the  $J_C$  and  $H_{C2}$  increases, the irradiation technique is not easily scalable for large scale production of long length conductors. So far chemical addition/doping is most suited and preferred method for the introduction of pinning centers in practical superconductors.

### **Chemical addition/doping for improving $J_C(H)$ and $H_{C2}$**

Chemical addition/doping, like in other practical superconductors is an effective and easy method for modifying the properties of MgB<sub>2</sub>. Doping may change the reaction kinetics, grain growth and hence the microstructure. Doping can cause crystalline and microstructural changes, create lattice defects/disorders and cause formation of non superconducting precipitates or inclusions in the superconductor matrix. All these defects can act as flux pinning centers and can increase the  $H_{C2}$  and  $H_{irr}$  values and hence enhance the in-field  $J_C$  of MgB<sub>2</sub>. A large number of additives/dopants have been introduced into MgB<sub>2</sub> aimed for the improvement of its superconducting properties. Some of them have negative effects, while most

have positive effect and a few significantly improved the superconducting properties in MgB<sub>2</sub>. Though it is not possible to describe all of them, an overview and summary of the effects of chemical addition/doping in MgB<sub>2</sub> is given here.

Various nano/submicron sized particles and materials having quite different physical and chemical properties were introduced into MgB<sub>2</sub>. These dopants include metallic elements, carbon (in various forms like nanopowders, nanotubes, graphite and diamond), carbides, silicides, borides, oxides and some hydrocarbons have been introduced into MgB<sub>2</sub> (see the extensive reviews [84, 85, 130–134] and references therein). These dopants improved the flux pinning and  $J_C(H)$  of MgB<sub>2</sub> to different extents. The final properties of doped MgB<sub>2</sub> depend on the chemical nature of the dopant and its distribution in the superconductor matrix. Generally carbon based dopants like nano C, SiC, B<sub>4</sub>C and some hydrocarbons etc give better  $J_C$  and  $H_{C2}$  in MgB<sub>2</sub> and nano SiC gives the best performance among the dopants [84, 85, 130–134]. Table 1.4 shows some of the types of dopants introduced on MgB<sub>2</sub>.

Table 1.4: Different types of additives/dopants added to MgB<sub>2</sub>. Data are taken from [84, 85, 130–133]

Metallic elements	Metal oxides	Hydrides Nitrides Borides Silicides	Carbon based		
			C (in different forms)	Carbides	Organic materials
Ti	MgO	Si <sub>3</sub> N <sub>4</sub>	nano C	SiC	Sugar
Zr	SiO <sub>2</sub>	WB	diamond	TiC	Paraffin
Ag	TiO <sub>2</sub>	ZrB <sub>2</sub>	graphite	WC	Malic acid
Al	Al <sub>2</sub> O <sub>3</sub>	NbB <sub>2</sub>	C nanotubes	B <sub>4</sub> C	Maleic anhydride
Fe	Fe <sub>2</sub> O <sub>3</sub>	TiB <sub>2</sub>	Silicon oil	NbC	Toluene
Cu	Co <sub>3</sub> O <sub>4</sub>	CaB <sub>6</sub>	Ca <sub>2</sub> CO <sub>3</sub>	Mo <sub>2</sub> C	Ethanol
Mo	Y <sub>2</sub> O <sub>3</sub>	WSi <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>		Acetone
Co	Ho <sub>2</sub> O <sub>3</sub>	ZrSi <sub>2</sub>			Tartaric acid
Ni	Dy <sub>2</sub> O <sub>3</sub>	Mg <sub>2</sub> Si			Ethyltoluene
La	Pr <sub>6</sub> O <sub>11</sub>	ZrH <sub>2</sub>			

Of the several metallic and non-metallic elements added into MgB<sub>2</sub> only C and Al entered into the lattice site: C substitutes at the B site and Al substitutes at the Mg sites. C substitution at B site altered the  $\sigma$  and  $\pi$  scat-

tering channels and strongly enhanced the  $H_{C2}$  and  $J_C(H)$  of MgB<sub>2</sub>. The metals Ti and Zr are reported to have some positive effect on the  $J_C(H)$  of MgB<sub>2</sub> [135, 136]. Ti is found to be a good grain refiner in MgB<sub>2</sub>, which absorbs the impurities (mainly oxides at grain boundaries) and hence improve the grain connectivity [137]. Similar results of grain refining have been observed with the dopants Zr, Ta and CaB<sub>6</sub> [85]. Materials like Mn and Fe are reported to substitute at Mg site, but only at very low concentrations. Being a magnetic material Fe doped as nano Fe reduced the  $J_C(H)$  of MgB<sub>2</sub> significantly [138]. While most of the other metals (Cu, Ag, Au, Ni ...) reacted with Mg/B to form intermetallics. These secondary phases reduces the grain connectivity and superconducting volume. So, many of these metallic dopants reduced the  $J_C(H)$  than enhancing [60].

As stated earlier C successfully enters into the B site and modifies the electronic and superconducting properties of MgB<sub>2</sub>. The substitution of C supplies one additional electron to the B plane, mean while due to the small covalent radii of C compared to B, the substitution locally distorts the lattice. This reduces the  $T_C$  with C substitution while enhances the scattering significantly. In MgB<sub>2</sub> the  $H_{C2}$  is strongly affected by the scattering and hence C substitution causes the  $H_{C2}$  to increase significantly. The lattice strains and distortions due to substitution can act as good flux pinning centers. Both these improve the  $J_C(H)$  in C substituted MgB<sub>2</sub> significantly. Today a typical C substituted MgB<sub>2</sub> tape has a  $J_C$  value  $> 10^4$  A/cm<sup>2</sup> at field 10-12 T and 4.2 K [139, 140], more than one order higher than that of undoped sample. C alloyed MgB<sub>2</sub> fibre showed a high  $H_{C2}$  of  $\sim 55$  T at 1.5 K [39] and  $\sim 70$  T is predicted for C doped thin films [82].

A significant breakthrough happened when Dou *et al* reported strong improvement in the  $J_C(H)$  by nano SiC addition [141–143]. Nano SiC improves the  $J_C(H)$  and  $H_{C2}$  of MgB<sub>2</sub> significantly, at all the temperatures, without decreasing the  $T_C$  much. Now nano SiC is the best dopant for MgB<sub>2</sub> superconductor which gives consistently high in-field  $J_C(H)$  values. In their work Dou *et al* [142] observed that compared to the undoped sample,  $J_C$  for the 10 wt% SiC doped sample is higher by a factor of 32 at 5 K and 8 T, 42 at 20 K and 5 T, and 14 at 30 K and 2 T. At 20 K and 2 T, the  $J_C$  for the doped sample is  $2.43 \times 10^5$  A/cm<sup>2</sup>, which is comparable to  $J_C$  values for the best Ag/Bi-2223 tapes. A typical nano SiC doped MgB<sub>2</sub> conductor has a  $J_C$  value higher than  $10^4$  A/cm<sup>2</sup> at 4.2 K and  $H_{C2}$  values of  $> 33$  T are reported for nano SiC doped wires [79]. Matsumoto *et al*

[144] reported a  $H_{C2}(0)$  value exceeding 40 T for SiC doped MgB<sub>2</sub> bulk samples, sintered at a temperature as low as 600 °C.

Compared with elemental C addition nano SiC needs only a lower reaction temperature for better C substitution. The doped samples have improved  $J_C(H)$  values both at low temperatures and high temperatures, without much reduction in  $T_C$ . Even for the 30 wt% of SiC addition  $T_C$  of MgB<sub>2</sub> is lowered by only 2.6 K [142], for C doping the  $T_C$  falls sharply with C content. The enhancement of  $J_C(H)$  in MgB<sub>2</sub> by SiC addition is explained by the dual reaction model [131, 132]. SiC decomposes and reacts with Mg (forms Mg<sub>2</sub>Si) for temperatures as low as 650 °C and release fresh C which subsequently substitutes at B site. The C substitution at B site enhances the scattering and hence the  $H_{C2}$ . The SiC addition results in a large number of nanometer sized (5-30 nm) dislocations within the MgB<sub>2</sub> grains [141, 142] and these dislocations can strongly pin the flux lines. When SiC reacts with liquid Mg and amorphous B at the reaction temperature, the nanoparticles of SiC will act as nucleation sites to form MgB<sub>2</sub>. The other nonsuperconducting reacted phases such as Mg<sub>2</sub>Si, BC, Si<sub>x</sub>B<sub>y</sub>O<sub>z</sub> along with unreacted SiC will be incorporated within the grains as inclusions [64, 141, 142]. These highly dispersed reaction-induced products also contribute to the flux pinning [141, 142]. Thus the improvement of both  $H_{C2}$  and flux pinning occurs as a result of SiC addition, which consequently enhances the in-field  $J_C$  significantly.

Realizing the strong positive influence of C on MgB<sub>2</sub> many groups tried various forms of C based dopants. These include nano carbon, carbon nanotubes (monowalled, double walled and multi walled), graphite and diamond. All these types resulted strong improvement in the  $H_{C2}$  and  $J_C$  of MgB<sub>2</sub>. In many of these dopants including nano C powder, a higher sintering temperature (900-1000 °C) favors better C incorporation into the lattice and better superconducting properties. One main limitation of C substitution is the reduction of  $T_C$  and hence a strong improvement of  $J_C(H)$  is obtained only in low temperatures (< 10 K). For higher temperatures (> 25 K) the enhancement is not very significant. Using nano C powder, graphite or diamond as a C source, the substitution of C for B cannot be achieved at the same temperature as that of the MgB<sub>2</sub> formation (around 650 °C). Higher sintering temperatures (900-1000 °C) favor better C substitution, but does not favor fine grains (weakens grain boundary pinning) and can cause more MgO formation. Nanosize precursor particles are expensive

and there are always agglomerations of the nano additives. Both these difficulties are reduced using hydrocarbons as the C source.

Now a lot of hydrocarbons including sugar, acetone, benzene, paraffin, toluene, ethanol, sterates, maleic acid etc are tried into MgB<sub>2</sub> with good results [84, 85, 130–133]. The main advantages of carbohydrates are their easy availability and low cost compared to the nano additives. They can be coated on the B powder surfaces with suitable solvent, giving better mixing with reduced agglomeration [145]. Even at lower temperatures carbohydrates melt and release fresh and highly reactive C for the substitution. The main drawback of carbohydrate addition is that most of them contain oxygen, which can easily react with Mg to form MgO which can degrade the grain connectivity and hence the critical current density.

Some silicides (ZrSi<sub>2</sub>, WSi<sub>2</sub>, Mg<sub>2</sub>Si), hydrides (ZrH<sub>2</sub>), and borides (TiB<sub>2</sub>, NbB<sub>2</sub>, ZrB<sub>2</sub>, WB) are also tried with moderate improvements in flux pinning and critical current density values [84, 85, 130–133]. These dopants are not incorporated into MgB<sub>2</sub> lattice. Si and silicides directly react with Mg. The reaction induced impurities as well as the added particles acts as flux pinning centers. A slight amount MgO in the MgB<sub>2</sub> grains is found to improve the flux pinning properties. Addition of metal oxides like Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub>, ZrO<sub>2</sub>, TiO<sub>2</sub> and SiO<sub>2</sub> are found to increase the MgO formation. However on the extend of  $J_C(H)$  improvement by these metal oxide additions, different works disagree with each other. Some reported decremental effect on  $J_C(H)$  by these oxides, while some reported some marginal benefits. The incorporation of nano rare earth (RE) oxides such as Y<sub>2</sub>O<sub>3</sub>, Ho<sub>2</sub>O<sub>3</sub>, Dy<sub>2</sub>O<sub>3</sub> and Pr<sub>6</sub>O<sub>11</sub> improved the flux pinning in MgB<sub>2</sub> [146–149]. In all these RE oxide additions the RE reacted with B to form their respective borides (YB<sub>4</sub>, HoB<sub>4</sub>, DyB<sub>4</sub> and PrB<sub>6</sub>). For the Y<sub>2</sub>O<sub>3</sub> doped sample  $J_C$  of  $\sim 2 \times 10^5$  A/cm<sup>2</sup> (at 2 T) and  $H_{irr}$  of 11.5 T are reported at 4.2 K and for Ho<sub>2</sub>O<sub>3</sub> addition  $J_C$  of  $\sim 1.2 \times 10^5$  are observed at 5 T, 5 K [146, 147].

Based on the performance of  $J_C(H)$  due to addition/doping, Dou *et al* [130–132] classified the additives/dopants in MgB<sub>2</sub> into four categories (groups). Table 1.5 summarizes the different categories of dopants and their effects on MgB<sub>2</sub>. The first group includes dopants like nano-SiC and carbohydrates which can have both reaction with Mg/B and C substitution. The second group includes materials such as nano-C, CNT and B<sub>4</sub>C which



Table 1.5: Classification of different categories of additives added to MgB<sub>2</sub>.

Group	Description	Typical additive	Improvement of $J_C(H)$	Main reason for affecting $J_C(H)$
1	C substitution and reaction with Mg/B	nano SiC, carbohydrates	Significant	C substitution <sup>a</sup> and pinning by the reaction induced impurities.
2	C substitution, but no reaction with Mg/B	nano C, CNT	Significant	C substitution. <sup>b</sup>
3	Reaction with Mg/B, but no C substitution	Silicides, Si, RE oxides	Moderate	Pinning by reaction induced impurities.
4	No C substitution and no reaction with Mg/B	BN, MgO	Slight improvement or decrement	Degrading grain connectivity.

<sup>a</sup> C substitution at the same temperature of MgB<sub>2</sub> formation.

<sup>b</sup> C substitution at higher temperature of MgB<sub>2</sub> formation.

can have C substitution without any reaction. The third group includes materials such as Si, Zr, Ti, RE oxides and silicides which can react with Mg/B without any C substitution, and the fourth group includes materials such as BN and MgO which do not have any reaction with Mg/B nor any C substitution. From the first group to the fourth group the enhancement of  $J_C(H)$  decreases gradually.

## 1.10 Objective of the present work

The brief overview presented above highlighted the importance of MgB<sub>2</sub> superconductor for practical applications. In order to exploit its full potential as a conductor it is essential to prepare long multifilamentary conductors in the form of wires, tapes or cables with good mechanical and superconducting properties. The research work presented in the thesis addresses some of the important issues on development of MgB<sub>2</sub> conductors for practical applications. The specific aims of the thesis are:

1. Development of good quality MgB<sub>2</sub> based superconductors in bulk, wire and tape geometries by simple and cost effective methods.
2. Improvement of the in-field critical current density of pristine MgB<sub>2</sub> superconductor by chemical addition.

Powder-In-Tube technique is found to be the most suitable method for the preparation of long length multifilamentary MgB<sub>2</sub> conductors. Several

aspects such as the feasibility of mechanical working (for rolling, drawing etc) and chemical compatibility with Mg and B must be studied for selecting suitable sheath/barrier materials. The quality of the final conductor is influenced by factors like initial packing density, heat treatment temperature and duration, number of filaments, core to sheath area etc. For better superconducting properties these factors must be optimized. For practical applications, superconductors with high in-field critical current density [ $J_C(H)$ ] are required. MgB<sub>2</sub> has a high self-field  $J_C$ , however, the  $J_C$  falls sharply in applied magnetic fields due to weak flux pinning. Significant research is being continued for the improvement of flux pinning and hence  $J_C(H)$ ,  $H_{irr}$  and  $H_{C2}$  in MgB<sub>2</sub>. Chemical addition/doping is an effective method for introducing flux pinning centers in a superconductor.

*In situ* PIT technique is used in the present work for preparing MgB<sub>2</sub> conductors. A systematic study on the chemical reactivity of various sheath materials with Mg/B is conducted for selecting the suitable material. After detailed investigations a systematic synthesis procedure is developed for the preparation of MgB<sub>2</sub> conductors using Fe as sheath, Cu as thermal stabilizer and Ni as outer sheath material. A novel, energy efficient and simple electrical self heating method is also developed for the preparation of sheathed MgB<sub>2</sub> conductors.

For improving the in-field  $J_C(H)$  of MgB<sub>2</sub> chemical addition with additives of different chemical and physical nature is carried out. A rare earth oxide, Tb<sub>4</sub>O<sub>7</sub> is added into MgB<sub>2</sub> first. Tb<sub>4</sub>O<sub>7</sub> addition improved the  $J_C(H)$  in MgB<sub>2</sub>, but the improvement was not drastic. Strong improvement in the  $J_C(H)$  of MgB<sub>2</sub> is reported for Carbon based nano materials. Especially, nano-SiC is reported to be one of the most effective additive for enhancing the  $J_C(H)$  of MgB<sub>2</sub>, by many groups. Based on the strong positive result of nano-SiC and other C based additives/dopants, studies are conducted on introduction of carbon containing additives/dopants into MgB<sub>2</sub>. In the present work a novel, inexpensive additive for C source, burned rice husk, is explored and excellent results are obtained. Combined addition of two materials with different chemical and physical properties are also investigated for further increasing the  $J_C(H)$ .

# Chapter 2

## Materials and methods

This chapter describes the general preparation and characterization techniques used in the study. Some of the descriptions are brief and will be expanded upon in the relevant chapters of the thesis.

### 2.1 Preparation techniques

In this study,  $\text{MgB}_2$  superconductor was prepared in bulk and wire/tape geometries. Wires/tapes are prepared and studied in mono and multi filamentary configurations. *In situ* preparation method was used for both the bulk and wires/tapes. Powders of Mg from GoodFellow (99.8%) and amorphous B from Merck (99%) are used for the preparations. Various metal/alloy tubes like Fe, Ni, Cu, SS, Monel also used for the present study.

#### 2.1.1 Bulk $\text{MgB}_2$ preparation

$\text{MgB}_2$  bulk superconductors were prepared by a Powder-In-Sealed-Tube (PIST) method. Mg and amorphous B powders were stoichiometrically mixed, mechanically compacted in stainless steel (SS) tubes, ends sealed and heat treated in air at 650-900 °C for different durations. After heat treatment the  $\text{MgB}_2$  bulk was recovered by mechanically removing the outer SS tube. Typical dimensions of PIST samples is 3 cm × 1 cm × 0.5 cm.

### 2.1.2 $\text{MgB}_2$ wire and tape preparation

$\text{MgB}_2$  wires and tapes were prepared by Powder-In-Tube (PIT) method. The processing steps are discussed in detail in chapter 4. For monofilamentary wire preparation, homogeneously mixed Mg and B powders were filled in Fe tubes of suitable dimensions and mechanically compacted. These powder filled tubes were then groove rolled to desired dimension. For mono filamentary tapes, the groove rolled wires were then flat rolled to the required dimensions. Photographs of groove and flat rolling machines used for the wire and tape rolling are shown in figure 2.1.

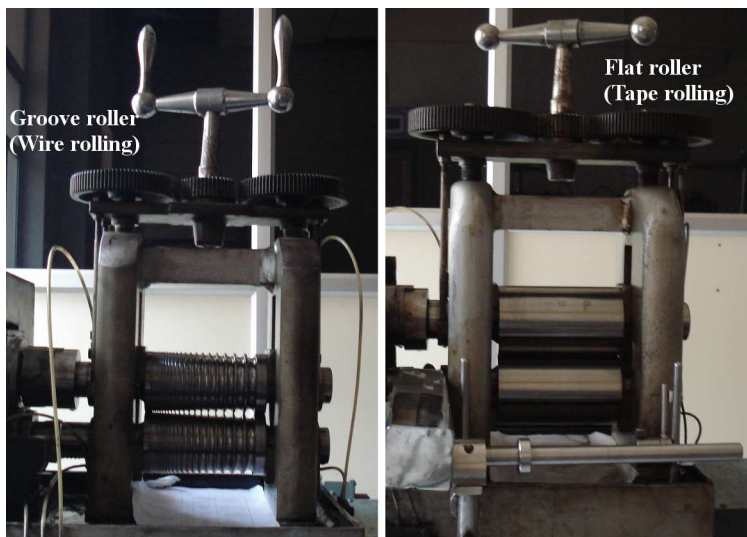


Figure 2.1: Photograph of rolling machines.

For multifilamentary conductors, as rolled mono wires were cut into small pieces and bundled together with Cu rods (stabilizer) and filled in suitable Ni tubes. These composites were then groove rolled for multifilamentary wires, followed by flat rolling for multifilamentary tapes. After rolling the ends of the wires/tapes were sealed by arc welding and then heat treated at  $650\text{-}750\text{ }^{\circ}\text{C}$  in air. A wet cloth was wound around the specimens during welding to avoid heating up of the samples. Short length wire samples for various characterizations were then selected by properly cutting out the reaction mixture area of the wire. The maximum length of multi-

filamentary wire prepared so far is about 5 m and the maximum number of filaments in multifilamentary wires is 10. Typical stabilized tape has the dimensions of  $\sim 1.2$  mm thickness and 3-4 mm width.

## 2.2 Structural characterization techniques

### 2.2.1 Phase and structural analysis : Powder XRD

X-ray diffraction is a very useful and easy method for the phase identification of crystalline materials. XRD data can be used for a semi-quantitative phase analysis. Besides the phase analysis XRD data gives useful information regarding the crystal lattice parameters, strain, grain size etc.

In the present study powder XRD patterns of samples were taken using a Philips X'pert Pro (Model No: PW 3040/60) X-ray diffractometer with Cu  $K_{\alpha}$  radiation employing X'Celerator and a monochromator at the diffracted beam side. The system has  $\theta - 2\theta$  Bragg-Bentano geometry with fully automated operation and data acquisition. Phase identification of the samples was performed using X'Pert Highscore software with support of the ICDD-PDF-2 database. The samples, either bulk or core of wire/tape were ground thoroughly to fine powder. The powder samples were filled in standard holders and the XRD data were recorded at room temperature. For less amount of powder (especially from small wires/tapes) a standard zero back ground holder is used. Appropriate slits were used to restrict the X-ray beam to the sample area. General scans were performed under 40 KV and 30 mA tube Voltage and Current values. Usually the samples were scanned for 21-85°  $2\theta$  values with a step size of  $< 0.02^{\circ}$ . The average scan takes about 20 minutes, while some slow scans were also performed in special cases.

The XRD data were analyzed for phase identification and lattice parameter calculations. The volume percentages of different phases in the samples were assessed semi-quantitatively, from the integrated X-ray peak intensities, using the relation

$$\text{Vol.\% of phase X} = \frac{\sum \text{Integrated peak intensities of phase X}}{\sum \text{Integrated peak intensities of all phases}}$$

The  $d$ -values of selected peaks of  $\text{MgB}_2$  were used for its lattice parameter calculations. Lattice parameters were calculated for the hexagonal crystal structure of space group  $p6/mmm$ , using the relation

$$\frac{1}{d^2} = \frac{4(h^2 + hk + k^2)}{3a^2} + \frac{l^2}{c^2}$$

The FWHM (full width at half maximum) of a XRD peak depends on factors like crystalline size, lattice strain and instrumental parameter etc. The FWHM of selected peaks of  $\text{MgB}_2$  were used for qualitatively assessing the lattice strain and grain size.

### 2.2.2 Microstructural analysis

#### Optical microscopy

In the present study optical microscopy is mainly used for analyzing the cross sectional features of the wires/tapes. The cross sectional analysis gives informations on the geometry, size, orientation, uniformity of the filaments and the interfaces between core/sheaths for the multifilamentary conductors. For the optical microscopy, samples of small size (1-2 cm) were cut from long conductors, polished mechanically and placed under the microscope in suitable holders. An OLYMPUS SZ-PT model microscope is used for the study and the samples were examined under magnification upto 30 X. Optical microscopy measurements, taken with the help of a scale built into the eyepiece, were used for the exact estimation of core and sheath cross sectional areas of mono/multifilamentary wires/tapes for determining the  $J_C$ . Some of the samples for SEM were pre-examined and short listed with the help of optical microscope.

#### Scanning Electron Microscopy

With greater resolution, higher magnification and large depth of focus Scanning Electron Microscopy (SEM) gives a detailed information of the microstructure of the sample. The SEM scan the sample with high energy electron beam in a raster scan pattern. The scan produces different signals including secondary electrons, back scattered electrons, characteristic X-rays, auger electrons etc, which contain the microstructural information of the sample. In the present study a JEOL JSM 5600LV system equipped with an x-ray energy dispersive spectrometer (EDS) was used for

secondary electron imaging (SEI) microstructural analysis. Typical magnification used was 5000 X or 10000 X, while other magnifications are also used for special cases. In most cases fractured surfaces were used, while polished surfaces were also used for some samples especially for wire/tape cross sectional analysis. The samples were mounted on a metal base using adhesive carbon tapes and loaded into the instrument. No gold coating was used for the superconducting  $\text{MgB}_2$  samples.

### **Transmission Electron Microscopy**

Compared with SEM, TEM has a higher magnification and resolution, allowing a more detailed microstructural examination. TEM diffraction patterns can be used to obtain precise structural information. TEM allows lattice scale imaging of the samples. In this study TEM is mainly used to get intra and inter grain features of sub micron or nano sized  $\text{MgB}_2$  particles and to determine the morphology, size and content of the nano size dopants. The instrument used was HRTEM FEI-Tecna  $G^2$  30 S-Twin 300 KV equipped with an X-ray energy dispersive spectrometer (EDS). For the TEM, samples were finely powdered, sonicated in acetone to remove agglomeration, and then placed on copper grids.

### **Energy Dispersive Spectroscopy**

Energy Dispersive Spectroscopy (EDS) allows a semi-quantitative elemental characterization of the samples. In the present study EDS analysis was done using automated EDS system integrated either to SEM or to TEM. The spectrum was taken either for a large area or for a single spot depending on the requirement. The limitation of EDS in the present study was its inability to accurately detect B because of its low atomic weight.

## **2.3 Superconducting characterization techniques**

The superconducting parameters  $T_C$ ,  $J_C$ ,  $J_C(H)$  and  $H_{irr}$  were measured using both transport and magnetic measurements for assessing the quality of samples. For transport measurements an indigenously designed cryostat integrated with an imported cryocooler is used. Figure 2.2 shows the schematic sketch of the cryocooler integrated cryostat. The cryocooler used is a Gifford-McMohan cooler manufactured by Sumititomo Heavy

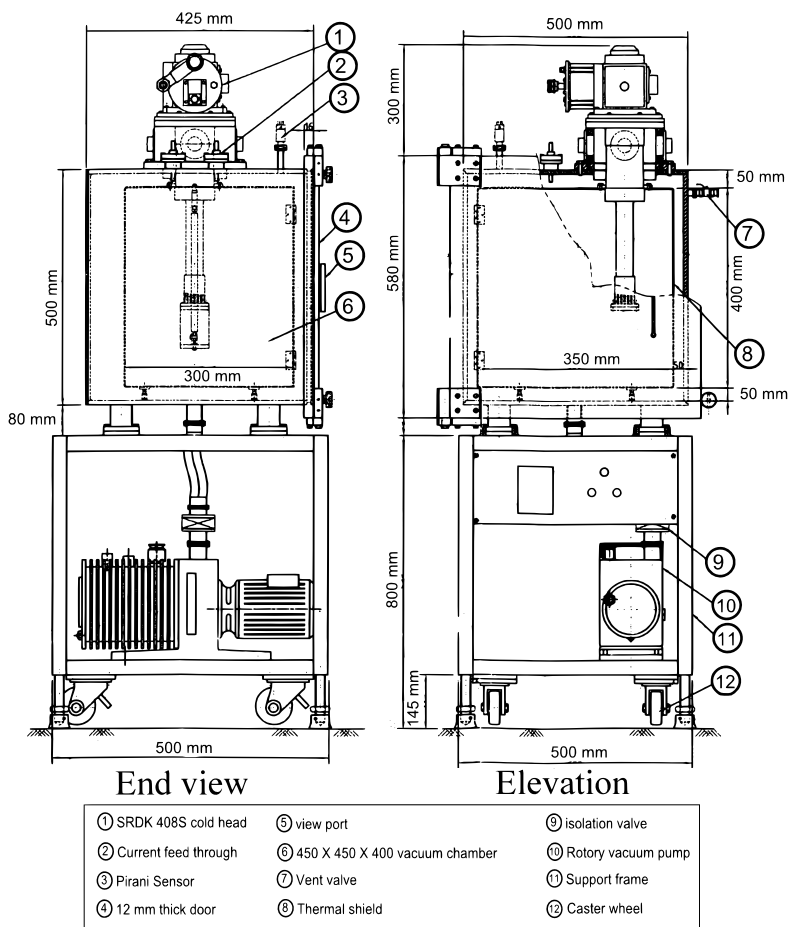


Figure 2.2: Schematic sketch of the cryocooler integrated cryostat.

Industries Ltd. The model number of compressor unit is CSW-71D and the cold head model is SRDK-408. Some of the wires and tapes were measured in liquid helium for transport properties at IPR, Gandhinagar. Magnetic measurements were done using a VSM or SQUID system in PPMS (Quantum Design, USA) with collaboration of RRCAT, Indore and JN-CASR, Bangalore. For transport measurements wire/tape samples were used while for magnetic measurements bulk samples were used.



### 2.3.1 Transport measurements

For transport measurements wires/tapes of 2-3 cm were properly anchored to the second stage of the cryocooler with a home made sample holder. Four probe resistivity method is used for the transport measurements. A schematic diagram of the four probe resistivity measurement arrangement is shown in figure 2.3. High quality insulated copper wires were used for current and voltage terminals. The leads from the terminals were directly soldered to the outer sheath using ortho phosphoric acid as a flux, after thoroughly cleaning the sheath surface with a sharp blade/knife edge.

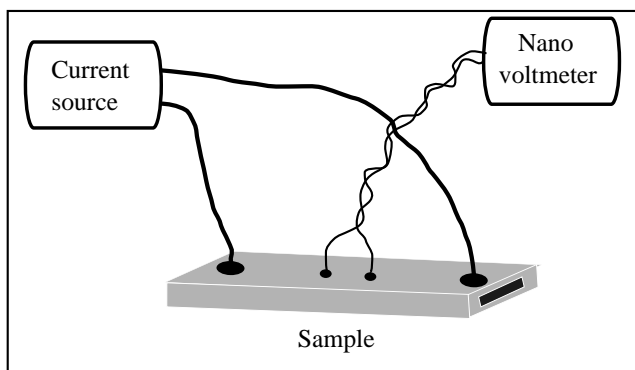


Figure 2.3: Schematic diagram showing the four probe resistivity setup.

Resistance-Temperature (R-T) and Current-Voltage (I-V) characteristics of the samples were measured to determine the  $T_C$  and  $I_C$ , of the samples. A programmable Keithley 220 current source and Keithley 181/2182A nano voltmeters were used for R-T measurements. A current of 10/100 mA was used for the R-T measurements. For I-V measurements programmable current sources of capacity 30/100/1000 A, manufactured by APLAB were used. All the R-T and I-V measurements were automated and controlled by a PC interfaced with the system through GPIB. Lakeshore L332/L340 model temperature controllers were used for monitoring and controlling the sample temperatures.

The temperature at which resistance falls sharply is taken as the  $T_C$  and the difference between the temperatures corresponding to the 90% and

10% of normal state resistivity ( $T_{C90}-T_{C10}$ ) is defined as  $\Delta T_C$  for the samples. From the I-V characteristics the current at which the voltage shows a sharp rise is defined as the transport  $I_C$ . Ratio of  $I_C$  to the total cross sectional area is taken as the engineering critical current density ( $J_E$ ) and the ratio of  $I_C$  to the cross sectional area of  $MgB_2$  core is taken as the critical current density ( $J_C$ ) for the samples. All the transport measurements (R-T and I-V) were automated using the GPIB interface.

### 2.3.2 Magnetic measurements

High field magnetic measurements for the present study were done in collaboration with RRCAT, Indore and JNCASR, Bangalore. Bulk samples of typical dimensions  $3 \text{ mm} \times 3 \text{ mm} \times 1.5 \text{ mm}$  were used for the measurements. The measurements were done with magnetic field applied along the longest dimension of the samples. M-T measurements were done at 100 Oe or at 25 Oe mainly in zero field cooling (ZFC) condition. M-H hysteresis loops were measured at 5 K (15 K also for some samples) upto 8 T.  $T_C$  of the sample is defined as the temperature at which the ZFC magnetization begin to fall in the M-T curve.  $\Delta T_C$  is taken as difference between temperatures corresponding to the 90% and 10% of the maximum shielding signal. Magnetic field dependence of the critical current density [ $J_C(H)$ ] of the sample was estimated based on Bean critical state model using the formula

$$J_C(H) = \frac{20 \times \Delta M}{a(1 - a/3b)}$$

where  $\Delta M$  (in  $\text{emu}/\text{cm}^3$ ) is the width of M-H loop, a and b (in cm) are dimensions ( $a < b$ ) perpendicular to the field, for a parallelepiped shaped sample.  $H_{\text{irr}}$  values of selected samples were estimated as the field at which  $J_C$  falls below  $100 \text{ A cm}^{-2}$ . The values of  $H_{\text{irr}}$  were estimated from Kramer plot also. For this the function  $J_C^{0.5} \times H^{0.25}$  plotted against  $H$  and  $H_{\text{irr}}$  was determined by linear extrapolation to zero of the Kramer curves.

## Chapter 3

# Preparation and characterization of $\text{MgB}_2$ bulk superconductor

For practical applications, it is required to prepare good quality bulk  $\text{MgB}_2$  with high phase purity, and acceptable superconducting properties. There are two main routes to prepare bulk  $\text{MgB}_2$  :- reaction of Mg and B sources (*in situ* technique) and the sintering of pre-reacted  $\text{MgB}_2$  powders (*ex situ* technique). The *ex situ* prepared samples generally have higher density and better homogeneity compared to the *in situ* samples. However for better superconducting properties, the *ex situ* samples need much higher sintering temperatures compared to the *in situ* samples. Further, doping of impurity elements has limitations in *ex situ* method.

Volatile Mg loss and Mg oxidation are two main hurdles for the *in situ* synthesis of  $\text{MgB}_2$ . Mg vapor loss at elevated temperature causes non-stoichiometry or B rich phases in the final product, and the  $\text{MgO}$  that forms at the grain boundaries acts as weak links. This affects the grain connectivity and reduces the critical current density of the superconductor [71]. Several synthesis procedures are reported for the preparation of *in situ*  $\text{MgB}_2$  bulks at relatively low temperatures with short durations of heat treatments [87–100]. The starting materials are Mg in powder/flakes/chips/lumps and amorphous/crystalline B in powder forms. In a few reports  $\text{MgH}_2$  powder is also used as Mg source [87, 88]. The bulk synthesis is done at

650-1000 °C for 30 min-5 hours heat treatment in vacuum/inert/reducing atmospheres.

We prepared bulk MgB<sub>2</sub> by a method designated herein as Powder-In-Sealed Tube (PIST) method, in which Mg and amorphous B powders were sealed inside stainless steel (SUS 304/SUS 316 L) tubes and heat treated. Stainless steel is chosen for the preparation of MgB<sub>2</sub> since it is non reactive with Mg and B at elevated temperatures and has adequate ductility and strength. The preparation route illustrated here can eliminate Mg evaporation loss and significantly reduce the oxidation of Mg, and reduce the cost of synthesis by avoiding expensive Nb/Ta tubes/foils, inert gases and special furnaces.

Parameters such as the temperature and duration of the heat treatment and the size of starting Mg powder were optimized for obtaining good quality MgB<sub>2</sub> bulk superconductor, in terms of phase purity, crystallinity and superconducting properties.

## **3.1 Preparation of MgB<sub>2</sub> bulk by Powder-In-Sealed-Tube (PIST) method**

### **3.1.1 Starting materials**

Mg powder from GoodFellow (99.8% pure) and amorphous B powder from Aldrich (99.0% pure) were used for the synthesis of *in situ* MgB<sub>2</sub> by the PIST method. Figure 3.1 shows the XRD patterns of starting Mg and B powders. Mg powder has good crystallinity and contained no detectable impurities including MgO. Though the B powder used is amorphous, it showed some small amount of crystalline phases. The observed crystalline phases are B in rhombohedral structure and a minor quantity of B<sub>2</sub>O. Figure 3.2 shows the SEM images of Mg and B powders used. B powder is very fine and homogenous in nature. The Mg powder is much bigger compared to the B powder and has irregular size and shape. Commercially available SUS 304/SUS 316 L stainless steel tubes of length 5-10 cm with different outside diameter (OD) and inside diameter (ID) (Typical OD/ID are : 12/10, 10/8, 6/4 : all in mm) were used for the filling of starting powders.

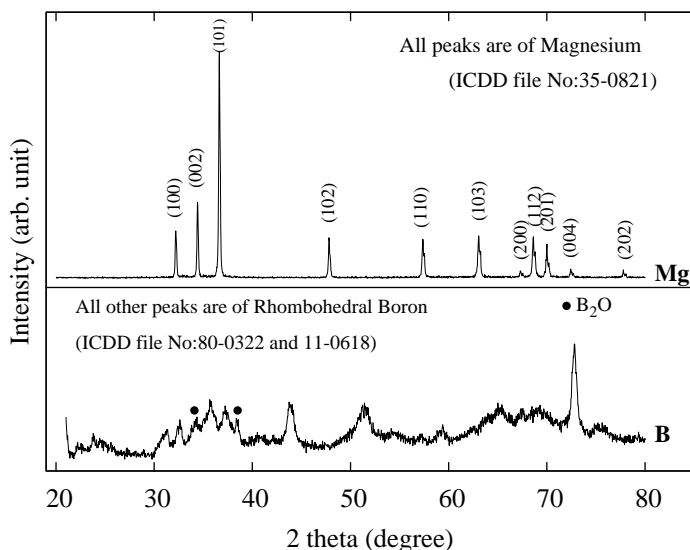


Figure 3.1: XRD pattern of the Mg and B starting powders.

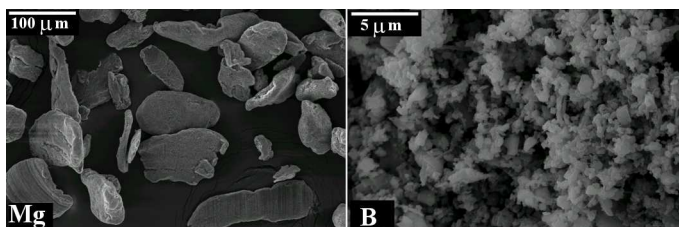


Figure 3.2: Secondary electron SEM image of starting Mg and B powders.

### 3.1.2 Sample preparation

Stainless steel (SUS 304) tubes of 10 cm long with an outside diameter (OD) of 6 mm and inside diameter (ID) of 4 mm were used for synthesis. One end of the tube was pressed uniaxially at a pressure of  $\sim 1$  GPa using a hydraulic press (HERZOG TP 20P) so that it became tape shaped. Stoichiometric weights of Mg powder and B powder were taken using an electronic balance (Mettler AE240). The powders were mixed, homogenized and ground thoroughly for about 1 hour using an agate mortar and

pestle. Then the powder mixture was densely packed through the open end of the pressed tube leaving some space unfilled. The unfilled portion was pressed with the same pressure that was used for the first end such that both ends are of equal length. Subsequently powder filled middle area was subjected to uniaxial pressing under 1 GPa to get a tape shaped portion. End sealing was performed by arc welding. A wet cloth was wound around the specimen during welding to avoid heating up of the sample.

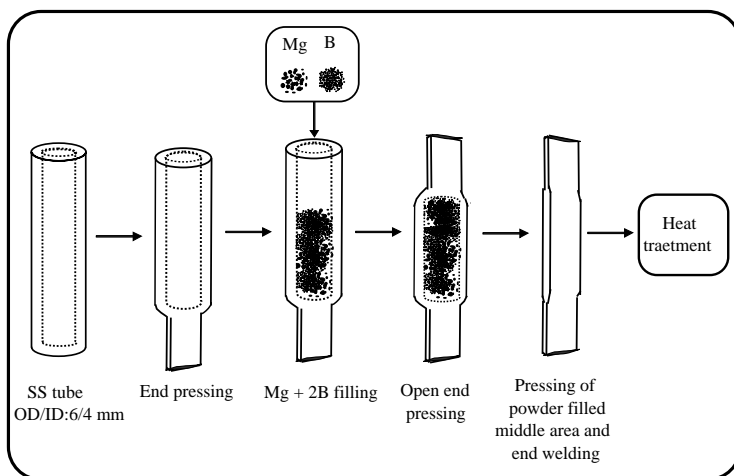


Figure 3.3: Schematic diagram of the preparation procedure in PIST method.

Figure 3.3 shows a schematic diagram of the sample preparation procedure. Figure 3.4 shows the photograph of a typical SS tube used for the filling of the powder and a powder filled sealed sample. Such samples were then heat treated in air at different temperatures and durations (typically  $670\text{ }^{\circ}\text{C}$ - $900\text{ }^{\circ}\text{C}$  for 0.5-10 hours) in a muffle furnace with a ramp rate of  $10\text{ }^{\circ}\text{C}/\text{minute}$  and subsequently furnace cooled. After heat treatment the outer SS sheath was mechanically removed and the  $\text{MgB}_2$  core was retrieved for characterizations.

### 3.1.3 Characterizations

The structural and phase analysis of the samples were performed using an X-ray Diffractometer (Philips X'pert Pro) with  $\text{Cu K}\alpha$  radiation employ-

ing X'Celerator and 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. Microstructural examination and elemental analysis of the samples were done by using an optical microscope (OLYMPUS SZ-PT), scanning electron microscope (SEM-JEOL JSM 5600LV) and transmission electron microscope (HRTEM FEI-Tecnai G<sup>2</sup> 30 S-Twin 300 KV) equipped with an X-ray energy dispersive spectrometer (EDS). DC magnetic measurements (M-T and M-H) were carried out by a vibrating sample magnetometer in Physical Property Measuring System (PPMS), Quantum Design, USA on samples having size 3 mm × 3 mm × 1.5 mm. Variation of resistance with temperature (R-T plot) were taken in a heavy duty closed cycle cryocooler-interfaced cryostat (Cold head Model : SHI SRDK-408) using DC four probe method.



Figure 3.4: Photograph of the bare and powder filled pressed SS tube (L ~ 10 cm, OD/ID = 6/4 mm).

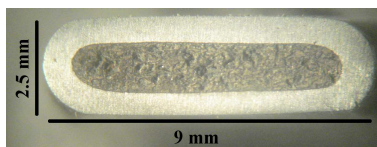


Figure 3.5: Optical photomicrograph of the transverse cross-sectional view of the polished surface of PIST sample after heat treatment.

### 3.1.4 Structural properties of PIST $\text{MgB}_2$

Figure 3.5 shows the optical micrograph of the cross-sectional view of the polished surface of SS sheathed  $\text{MgB}_2$  processed at 850 °C for 2 hours. The core layer is observed to be dense and black. The interface region

between  $\text{MgB}_2$  core and SS tube is sharp and distinct and there is no sign of any interfacial reaction occurring between the core and the sheath at this temperature.

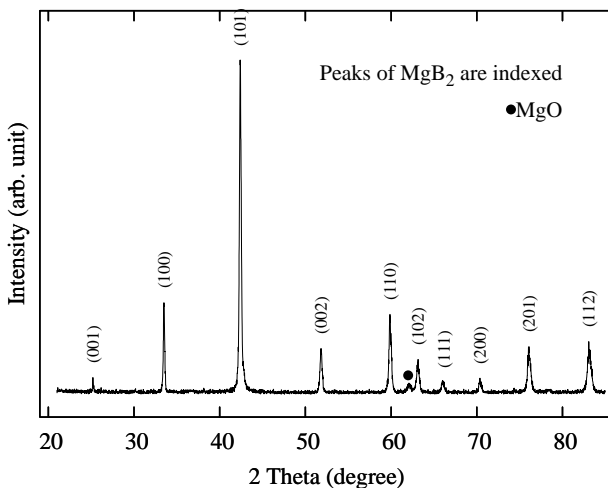


Figure 3.6: Powder XRD pattern of PIST  $\text{MgB}_2$ .

Figure 3.6 shows a typical XRD spectrum of the  $\text{MgB}_2$  core heat treated at  $850^\circ\text{C}$  for 2 hours. Crystalline  $\text{MgB}_2$  is the main phase with only a trace of  $\text{MgO}$  as the impurity phase. The sharp peaks of  $\text{MgB}_2$  is indexed to the hexagonal crystal structure of ICDD file number 38-1369. The very small amount of  $\text{MgO}$  observed is due to the air entrapped inside the tube before sealing the ends. No boron rich phases such as  $\text{MgB}_4$  or  $\text{MgB}_7$  are observed which ensures complete suppression of  $\text{Mg}$  evaporation loss during the heat treatment.

The lattice constants of the prepared  $\text{MgB}_2$  phase were determined from the XRD data, considering the hexagonal crystal structure and the values are  $a = 3.0862 \text{ \AA}$ ,  $c = 3.5260 \text{ \AA}$ , consistent with reported values for  $\text{MgB}_2$  [11, 21]. The geometric density of the bulk  $\text{MgB}_2$  was determined by measuring the mass and dimensions of rectangular shaped pieces cut from the  $\text{MgB}_2$  core. The PIST samples have high level of porosity and hence have a low average density of  $\sim 1.3 \text{ g/cc}$  ( $\sim 50\%$  of the theoretical density).



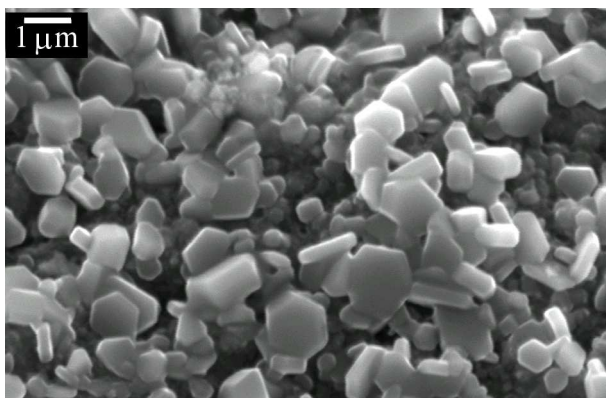


Figure 3.7: Secondary electron SEM image of PIST MgB<sub>2</sub>.

Figure 3.7 shows a typical secondary electron SEM image of the fractured surface of PIST MgB<sub>2</sub> heat treated at 850 °C. The microstructure of the sample is homogeneous in nature. The sample shows fine faceted hexagonal and randomly oriented MgB<sub>2</sub> grains of varying sizes. The grains have sizes varying around 1 μm. The EDS analysis of a typical sample is shown in figure 3.8. The EDS shows the presence of Mg, B and traces of O in the grains, which is in agreement with the XRD results.

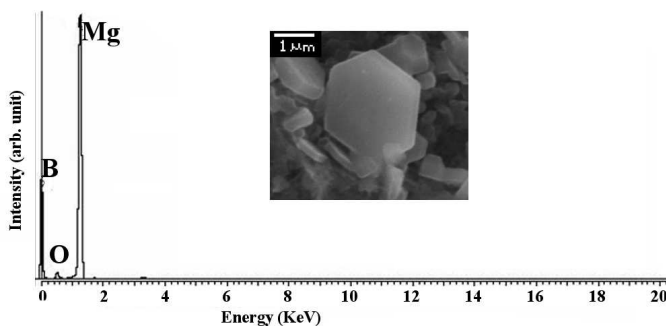


Figure 3.8: EDS spectrum of typical PIST MgB<sub>2</sub>. Inset of the figure shows the hexagonal MgB<sub>2</sub> grain.

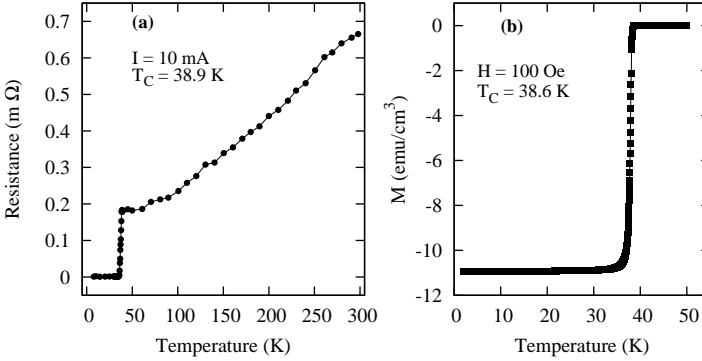


Figure 3.9: Temperature dependence of (a) resistance ( $R$ - $T$ ) and (b) magnetization ( $M$ - $T$ ) curves of PIST MgB<sub>2</sub>.

### 3.1.5 Superconducting properties of PIST MgB<sub>2</sub>

Both transport and magnetic measurements show sharp superconducting transition with  $T_C = 38$ – $39$  K and  $\Delta T_C < 1$  K for the PIST MgB<sub>2</sub>. Figure 3.9 (a) shows the temperature dependency of resistance ( $R$ - $T$  plot) in the temperature range 8– $300$  K, of a typical bulk MgB<sub>2</sub> measured using a closed cycle cryocooler. The MgB<sub>2</sub> shows superconducting transition at  $38.9$  K. Zero field cooled (ZFC) magnetization plot in the temperature range 2 to  $50$  K, taken at  $100$  Oe is shown in figure 3.9 (b). The sample show sharp superconducting transition with  $T_C$  around  $38.6$  K and  $\Delta T_C < 1$  K. The consistently high  $T_C$  and small  $\Delta T_C$  values show that the sample has excellent crystallinity and good homogeneity.

The field dependent magnetization ( $M$ - $H$  plot) of a typical PIST MgB<sub>2</sub> sample is shown in figure 3.10. Thermo-magnetic flux jumps are observed for fields below  $2$  T for the sample without any dopants at  $5$  K, as observed in many previous reports [60, 150–152]. The flux jump occurs only under conditions of extremely high critical currents, high magnetic diffusivity and low heat capacity causing localized motion of magnetic flux. In MgB<sub>2</sub>, since the magnetic diffusivity into the sample is much larger than the thermal one, flux jump is considered as a process of magnetic diffusion. The temperature of the sample increases during flux jump and the sample may transit from superconducting state to normal state. Flux jump is more at lower temperatures. At  $15$  K no flux jump is observed.

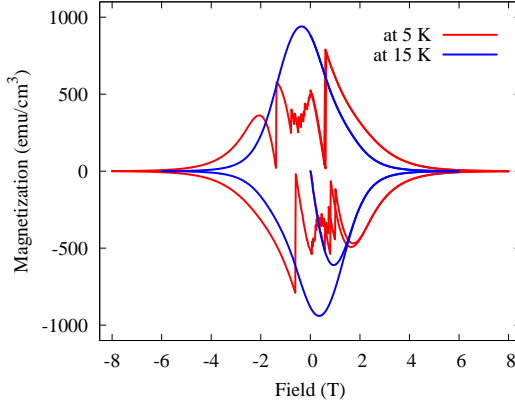
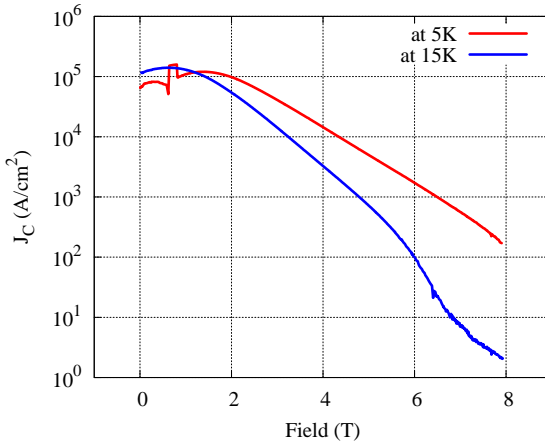
Figure 3.10: M-H plot of a typical PIST MgB<sub>2</sub>.Figure 3.11: Magnetic  $J_C(H)$  characteristics of typical PIST MgB<sub>2</sub>.

Figure 3.11 shows the field dependence of a magnetic critical current density [ $J_C(H)$ ] of typical PIST MgB<sub>2</sub> sample at 5 K and 15 K, deduced from M-H data. The  $J_C(H)$  is estimated based on Bean critical state model using the formula. At 5 K, at lower fields the estimation of  $J_C$  is not accurate due to flux jumps. At 5 K the magnetic  $J_C$  is  $\sim 10^5$  A/cm<sup>2</sup> at 2 T and  $\sim 0.8 \times 10^4$  A/cm<sup>2</sup> at 5 T. At 15 K the  $J_C$  is  $\sim 6 \times 10^4$  A/cm<sup>2</sup> at 2 T

and  $\sim 5 \times 10^3$  A/cm<sup>2</sup> at 5 T. The  $H_{\text{irr}}$  of the sample, defined as the field at which  $J_C$  falls below 100 A/cm<sup>2</sup> is higher than 8 T at 5 K and is  $\sim 6$  T at 15 K. All these values are comparable with many of the good quality MgB<sub>2</sub> bulks reported worldwide. Table 3.1 summarizes the properties of bulk MgB<sub>2</sub> prepared by PIST method.

Table 3.1: Features of PIST method.

Main advantages	No vacuum or inert atmosphere needed and reduced Mg oxidation and vapor loss
Starting materials	Mg and B in powder form
Filling tube	SS 304/SS 316 L
Sealing	By arc welding
Heat treatment	800-850 °C in air
Impurities in the final samples	Only traces of MgO
Average MgB <sub>2</sub> grain size	1 μm
$T_C$	38-39 K
$J_C$	$> 10^5$ A/cm <sup>2</sup> at 2 T, 5 K $> 10^4$ A/cm <sup>2</sup> at 2 T, 15 K and $> 10^3$ A/cm <sup>2</sup> at 5 T, 15 K
$H_{\text{irr}}$	$> 8$ T at 5 K, $\sim 6$ T at 15 K
$F_{\text{Pmax}}^*$	1-2 GN/m <sup>3</sup> at 5-15 K

\*  $F_{\text{Pmax}}$  is the maximum flux pinning force density.

## 3.2 Optimization of preparation conditions

For *in situ* synthesized MgB<sub>2</sub>, the  $J_C(H)$ ,  $H_{\text{irr}}$  and  $H_{C2}$  depends sensitively on factors like chemical composition, homogeneity, density, microstructure, grain connectivity and flux pinning of the sample. These factors are influenced by the process conditions, as well as the purity, size and nature of starting raw powders [83, 92, 93, 153–157].

For the *in situ* MgB<sub>2</sub> bulk, based on the synthesis method and nature of starting materials many reported heat treatment at 700-850 °C for 30 min-5 hours for optimized superconducting properties. A low synthesis temperature/duration favors fine sized grains, enhancing grain boundary pinning, at the cost of incomplete reaction, reduced crystallinity and or low lattice substitution (for the case of doping). Higher synthesis temperature/duration causes grain growth, improves crystallinity and level of substitution at the expense of low grain boundary pinning and increased MgO formation. So an optimum preparation condition has to be needed for detailed studies.

### 3.2.1 Effect of heat treatment conditions on structural properties

Samples heat treated in air at 700 °C, 800 °C, and 900 °C for 1, 2, 5 and 10 hours were prepared by *in situ* PIST method. Crystalline and microstructural characterization of the samples are done using XRD and SEM studies.

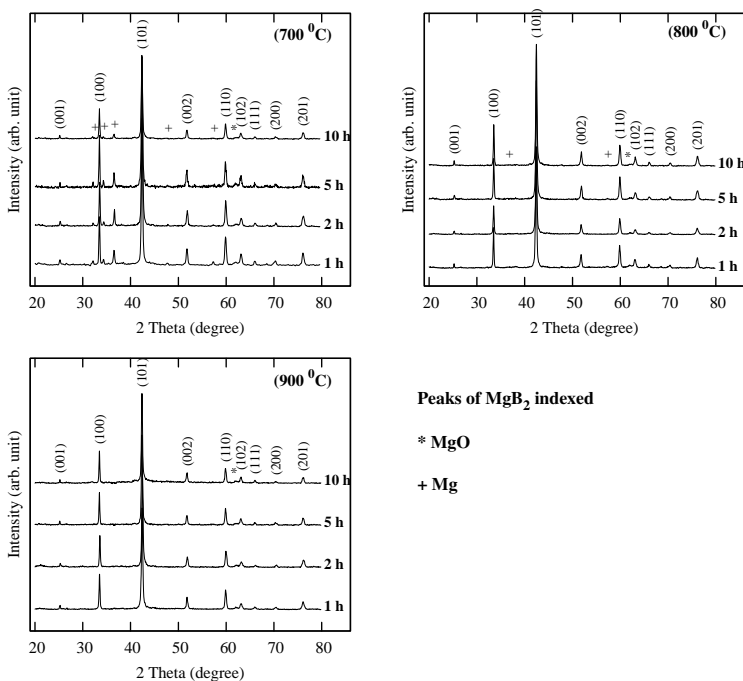


Figure 3.12: Powder XRD patterns of the samples heat treated at 700 °C, 800 °C and 900 °C for 1, 2, 5 and 10 hours.

Powder XRD patterns of the samples heat treated at 700 °C, 800 °C, and 900 °C for 1-10 hours are shown in figure 3.12. Crystalline MgB<sub>2</sub> is the major phase observed in all the samples, with traces of MgO. Unreacted Mg is observed in some samples heat treated at 700 °C and 800 °C for lower sintering durations. The amount of unreacted Mg decreases and crystalline MgB<sub>2</sub> increases with increasing heat treatment durations.

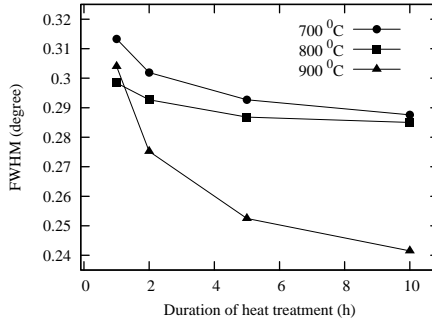


Figure 3.13: FWHM of (101) peak of the samples heat treated at 700 °C, 800 °C and 900 °C for 1, 2, 5 and 10 hours.

Figure 3.13 shows the full width at half maximum (FWHM) of (101) peaks of the samples. The figure clearly shows that the FWHM decreases with increase in the temperature of synthesis. The FWHM decreases more sensitively with increase in the duration of heating. The decrease in FWHM is more for samples heated at 900 °C. The decrease in the FWHM indicates the increase in the MgB<sub>2</sub> grain size, with increase in heating temperature and duration.

Table 3.2: Lattice parameters of the samples, calculated from XRD data

Heat treatment	Heat treatment temperature (°C)					
	700		800		900	
Duration (h)	<i>a</i> (Å)	<i>c</i> (Å)	<i>a</i> (Å)	<i>c</i> (Å)	<i>a</i> (Å)	<i>c</i> (Å)
1	3.085	3.526	3.088	3.534	3.088	3.522
2	3.086	3.525	3.088	3.522	3.089	3.519
5	3.084	3.526	3.086	3.523	3.089	3.532
10	3.086	3.524	3.086	3.529	3.086	3.522

Table 3.2 shows the lattice parameters *a* and *c* of the samples, calculated from the XRD data. The lattice parameters of the samples show no significant variations within the experimental error.

Figure 3.14 shows the secondary electron SEM images of the samples heat treated at 700 °C, 800 °C and 900 °C for 1 and 10 hours. The mi-

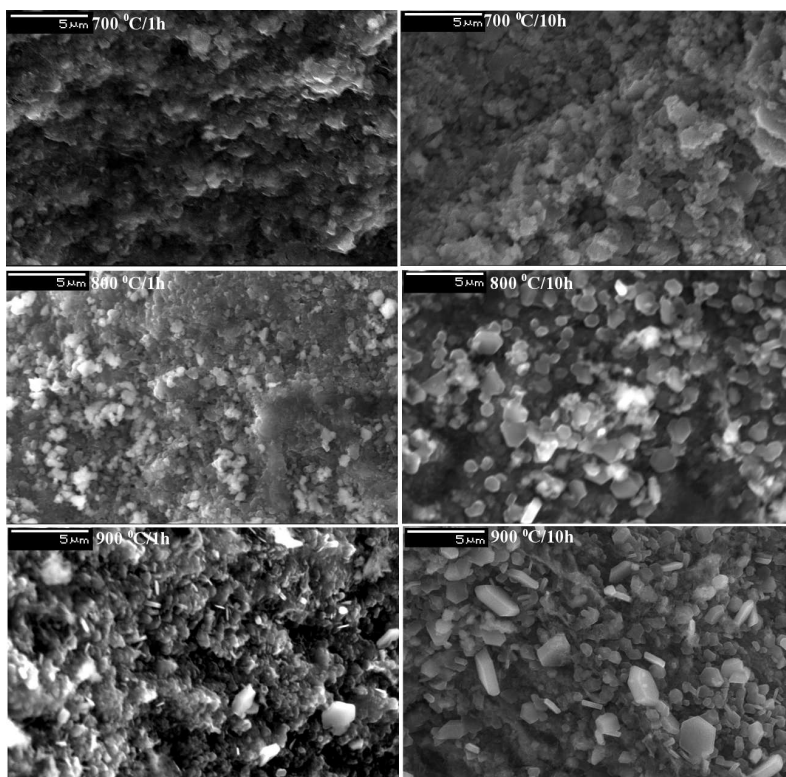


Figure 3.14: Secondary electron SEM images of the samples heat treated at 700 °C, 800 °C and 900 °C for 1 and 10 hours.

crostructure of all the samples is homogeneous in nature. The samples show fine hexagonal  $\text{MgB}_2$  grains of varying sizes. SEM images show that the average grain size and grain connectivity of the samples are improved with increase in sintering temperature. The grain size also improves with the sintering duration, for each sintering temperature. The information from the SEM images are in good agreement with the FWHM of the samples shown in figure 3.13.

The results indicate that both the sintering temperature and duration of sintering have influence on the crystalline and microstructural properties of *in situ* polycrystalline  $\text{MgB}_2$ . As the sintering temperature and its duration

increase the amount of crystalline  $\text{MgB}_2$  increases. The average grain size of crystalline  $\text{MgB}_2$  increases with increasing the sintering temperature and durations.

### 3.2.2 Effect of heat treatment temperature on the superconducting properties

Based on the above results on the crystalline and microstructural properties, four samples were prepared for superconducting measurements. The samples were heat treated at 750 °C, 800 °C, 850 °C, and 900 °C for 2 hours. The samples were named as MB750, MB800, MB850 and MB900 respectively.

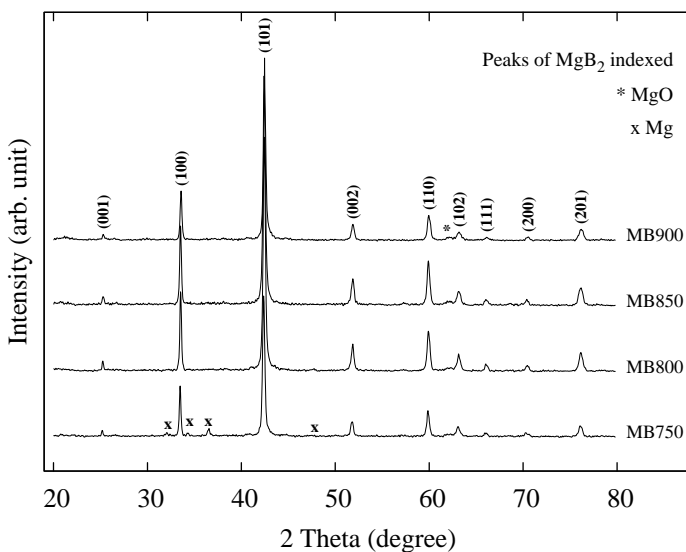


Figure 3.15: Powder XRD patterns of the samples heat treated at 750 °C, 800 °C, 850 °C and 900 °C for 2 hours.

Powder XRD patterns of the samples are shown in figure 3.15.  $\text{MgB}_2$  is the main phase and small amount of  $\text{MgO}$  is observed in all the samples. Small amount of unreacted residual  $\text{Mg}$  is detected for the sample



heat treated at 750 °C. No peaks of MgB<sub>4</sub> or other higher borides are observed in any of the samples. The very small quantity of MgO observed is due to the entrapped air before end-sealing of the tubes. Table 3.3 shows the lattice parameters  $a$ ,  $c$  axes, unit cell volume and the full width at half maximum (FWHM) of the (110) and (002) peaks of the samples. FWHM of both the peaks decreases significantly with increasing sintering temperature, indicating increase in MgB<sub>2</sub> grain size with sintering temperature.

Table 3.3: Lattice parameters and FWHM of the samples, calculated from XRD data

Sample	$a$ (Å)	$c$ (Å)	Cell volume (Å <sup>3</sup> )	FWHM (degree) of peaks	
				(002)	(110)
MB750	3.086	3.524	29.070	0.328	0.327
MB800	3.088	3.521	29.073	0.306	0.317
MB850	3.087	3.523	29.081	0.286	0.308
MB900	3.090	3.519	29.089	0.256	0.237

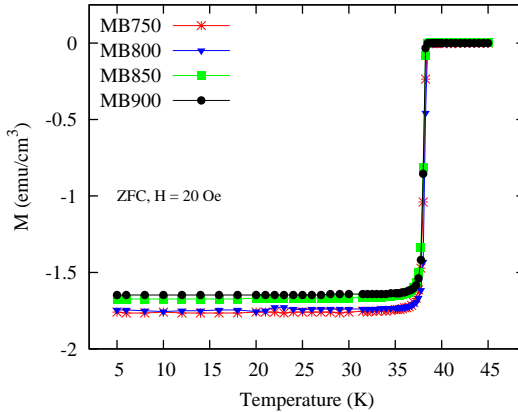


Figure 3.16: M-T plots of the samples heat treated at 750 °C, 800 °C, 850 °C and 900 °C for 2 hours.

Temperature dependence of magnetization (M-T) at 20 Oe of the samples is shown in figure 3.16. All the samples show sharp superconducting transition with  $T_C$  around 38.5 K and  $\Delta T_C \sim 0.8$  K. The almost identical

$T_C$  and  $\Delta T_C$  values indicate that the samples are identical with respect to stoichiometry, lattice or structural defects and the electronic states in the superconducting B planes.

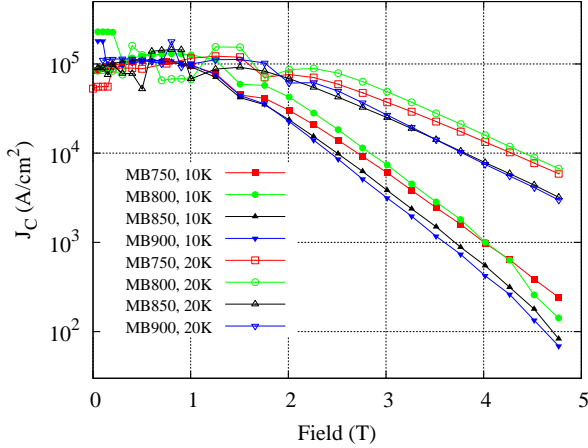


Figure 3.17:  $J_C(H)$  plots of the samples heat treated at 750 °C, 800 °C, 850 °C and 900 °C for 2 hours.

The in-field critical current density [ $J_C(H)$ ] at 10 K and 20 K, estimated from the M-H curves is shown in figure 3.17. At 10 K, and at low fields  $J_C$  jumps abruptly due to the flux jumps. But at higher fields the  $J_C(H)$  follows systematic behavior for all the samples. Sample heat treated at 800 °C shows higher  $J_C$  in external fields, at both 10 K and 20 K. In general, the  $J_C(H)$  is better for samples heat treated at low sintering temperatures (750 °C and 800 °C), while it is lower for samples heat treated at relatively higher temperatures (850 °C and 900 °C). The slightly higher  $J_C(H)$  of the samples MB750 and MB800 is mainly due to the smaller grains.

Thus the critical temperature of the MgB<sub>2</sub> remains almost same for samples prepared at different temperatures, while  $J_C(H)$  is slightly higher for samples prepared at relatively lower temperatures.

### 3.2.3 Effect of Mg particle size

In this section the role of Mg particle size on the reactivity of Mg with B was studied. The samples were synthesized using Mg particles of four different size categories. The superconducting properties of selected samples were evaluated for finding an optimum Mg particle size.

#### Effect on reaction between Mg and B

At first two sets of samples-one set with Mg particle size 25-53  $\mu\text{m}$  (+500 to -300 mesh) and other 106-180  $\mu\text{m}$  (+150 to -85 mesh)- were prepared. For all the samples B powder used was of size < 44  $\mu\text{m}$  (-325 mesh). The two sets of the samples were prepared at 700, 800, 850 and 900 °C for 2 and 10 hours. The samples were then characterized using powder XRD analysis. The samples prepared using smaller and larger Mg particles were named as MB S and MB L respectively.

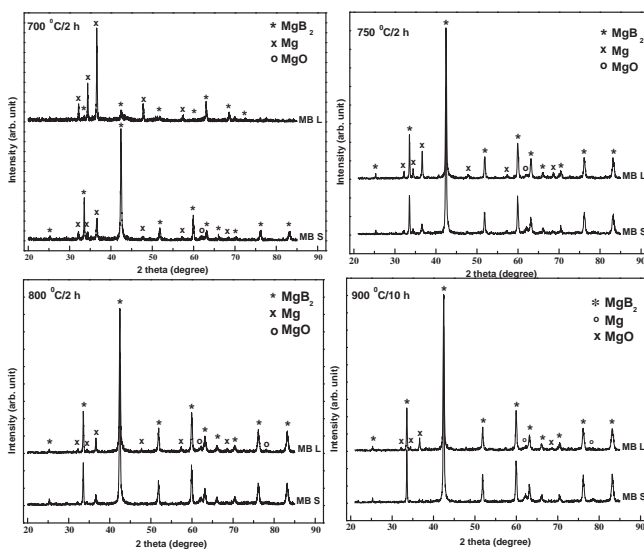


Figure 3.18: Powder XRD patterns of MB S and MB L heated at different temperatures and durations.

Powder XRD patterns of the samples MB S (Mg size: 25-53  $\mu\text{m}$ ) and MB L (Mg size: 106-180  $\mu\text{m}$ ) at different heat treatment temperatures (700-900  $^{\circ}\text{C}$ ) and durations (2 and 10 hours) are shown in figure 3.18. Quantitative data of various phases formed (MgB<sub>2</sub>, MgO and remnant Mg) are shown in table 3.4. MgB<sub>2</sub> is the main phase and small amounts of MgO and remnant Mg are observed for MB S. However, for MB L, remnant Mg is much higher and the amount of MgB<sub>2</sub> is lower compared to MB S. Most importantly, at 700  $^{\circ}\text{C}$  / 2 h, the amount of MgB<sub>2</sub> is very low and the remnant Mg is high for MB L.

Table 3.4: Volume percentage of MgB<sub>2</sub>, MgO and Mg in MB S and MB L heat treated at different temperatures and durations.

Heat treatment	Volume percentage of (%)					
	MgB <sub>2</sub>		MgO		Mg	
	MB S	MB L	MB S	MB L	MB S	MB L
700 $^{\circ}\text{C}$ /2h	82.01	14.67	0.42	0.00	17.57	85.33
750 $^{\circ}\text{C}$ /2h	91.11	84.20	2.15	0.89	6.74	14.91
800 $^{\circ}\text{C}$ /2h	93.13	90.53	2.25	2.11	4.62	7.36
850 $^{\circ}\text{C}$ /2h	97.46	93.44	2.54	1.16	0.00	5.40

To find the more usable Mg particle size for better superconducting properties four more samples were prepared with different Mg particle sizes. The Mg particles sizes used were < 25  $\mu\text{m}$ , 25-53  $\mu\text{m}$ , 53-106  $\mu\text{m}$  and 106-180  $\mu\text{m}$ . The samples were heat treated at 850  $^{\circ}\text{C}$  for 2 hours. The samples were named as MB1 (Mg size: < 25  $\mu\text{m}$ ), MB2 (Mg size: 25-53  $\mu\text{m}$ ), MB3 (Mg size: 53-106  $\mu\text{m}$ ) and MB4 (Mg size: 106-180  $\mu\text{m}$ ) respectively. Powder XRD patterns of the samples are shown in figure 3.19. Residual Mg is detected for all samples except MB1 and its amount increases significantly with increase in the starting Mg particle size. No peaks of MgB<sub>4</sub> or other higher borides are observed in any of the samples. There may be unreacted amorphous B, but cannot be detected in XRD. The very small quantity of MgO observed is due to the entrapped air before end-sealing of the tubes. The starting Mg powders were free from oxygen as their XRD patterns showed no MgO within the detection limit.

Quantitative phase analysis of the samples is shown in table 3.5. From the table it is clear that both MgB<sub>2</sub> and MgO are higher for samples synthesized from smaller sized Mg powders (MB1 and MB2). As the particle

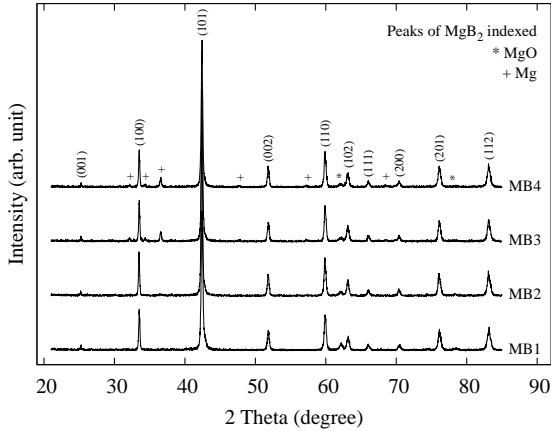


Figure 3.19: Powder XRD patterns of the samples MB1, MB2, MB3 and MB4 heated at  $850\text{ }^\circ\text{C}/2\text{h}$ .

size of starting Mg powder increases, both  $\text{MgB}_2$  and MgO decrease and the residual Mg increases (MB3 and MB4). For MB1 and MB2 the initial Mg particle size ( $< 25\text{ }\mu\text{m}$  for MB1 and  $25\text{-}53\text{ }\mu\text{m}$  for MB2) is comparable with that of B ( $< 44\text{ }\mu\text{m}$ ). For MB3 and MB4 the initial Mg particle size ( $53\text{-}106\text{ }\mu\text{m}$  for MB3 and  $106\text{-}180\text{ }\mu\text{m}$  for MB4) is significantly higher compared to the B powder. This clearly shows that the amount of residual Mg increases significantly as the Mg particle size increases above the B particle size.

Table 3.5: Volume percentage of  $\text{MgB}_2$ , MgO and Mg in MB1, MB2, MB3 and MB4 heat treated at  $850\text{ }^\circ\text{C}/2\text{h}$ .

Sample	Volume percentage of (%)		
	$\text{MgB}_2$	MgO	Mg
MB1	97.40	2.60	0.00
MB2	98.04	1.44	0.52
MB3	93.83	1.12	5.05
MB4	93.08	1.04	5.87

Figure 3.20 shows the secondary electron SEM images of the samples. The samples show distinct difference in microstructure with respect to Mg

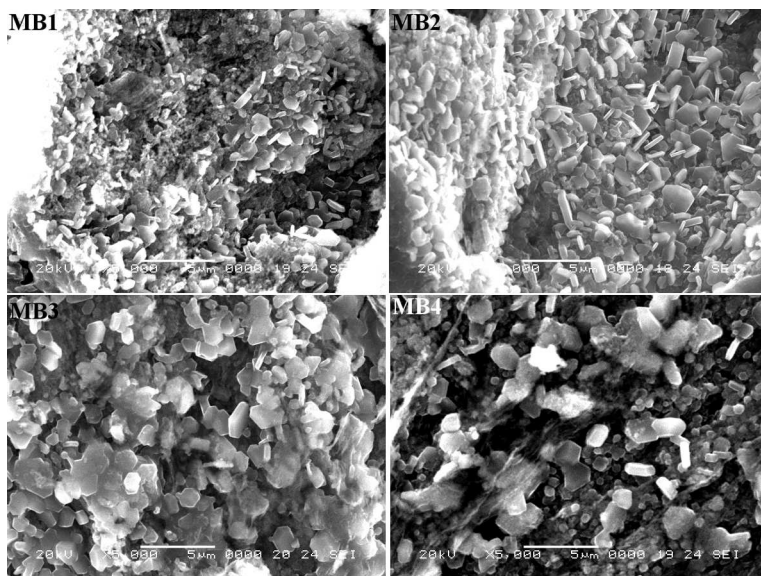


Figure 3.20: SEM images of MB1, MB2, MB3 and MB4 heated at 850 °C/2h.

particle size. Samples MB1 and MB2 show homogeneous microstructures with randomly oriented hexagonal  $\text{MgB}_2$  grains of varying size. The grains are densely packed and the average grain size is around 1  $\mu\text{m}$ . All the grains are well connected and sharp grain boundaries can be seen for higher sized grains. But for MB3 and MB4 the microstructure is less homogeneous with larger grain size compared with those of MB1 or MB2, and contain significant amount of amorphous like regions. In MB3 and MB4 hexagonal grains of different sizes are loosely packed and the grains are not well connected as those of MB1 and MB2. Some of the hexagonal grains of MB4 have notably high grain sizes. A significant portion of the MB4 contains amorphous like (or less crystallized) regions.

The full width at half maximum (FWHM) of (101), (002) and (110) peaks for the samples is shown in figure 3.21, which clearly indicates higher FWHM for MB1, implying reduced  $\text{MgB}_2$  grain size in this sample, in accordance with the SEM images.

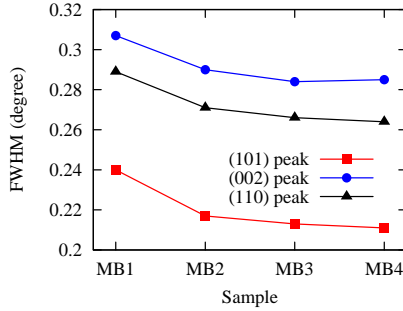


Figure 3.21: FWHM of (101), (002) and (110) peak of the samples.

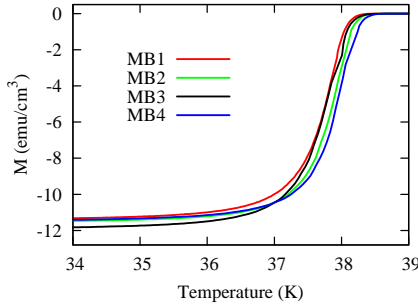


Figure 3.22: M-T plots of MB1, MB2, MB3 and MB4 heated at 850 °C/2h.

### Effect on the superconducting properties of $\text{MgB}_2$

In order to study the influence of Mg particle size on the superconducting properties of  $\text{MgB}_2$  with Mg particle size the samples MB1, MB2, MB3 and MB4 further characterized using DC magnetization measurements. Temperature dependence of magnetization (M-T) of the samples is shown in figure 3.22. All the samples show sharp superconducting transition with  $T_C$  in the range 38.4-38.6 K and  $\Delta T_C$  ( $T_{C90\%} - T_{C10\%}$ )  $\sim$  1.1-1.2 K. The almost identical  $T_C$  and  $\Delta T_C$  values of the samples indicate that unreacted Mg or B do not cause any significant change in the superconducting transition temperature of  $\text{MgB}_2$ . This is consistent with the earlier studies on the  $\text{Mg}_x\text{B}_2$  samples, in which  $T_C$  was found to be nearly constant, with a spread of only 0.3 K for  $0.6 < x < 1.3$  [93, 158].

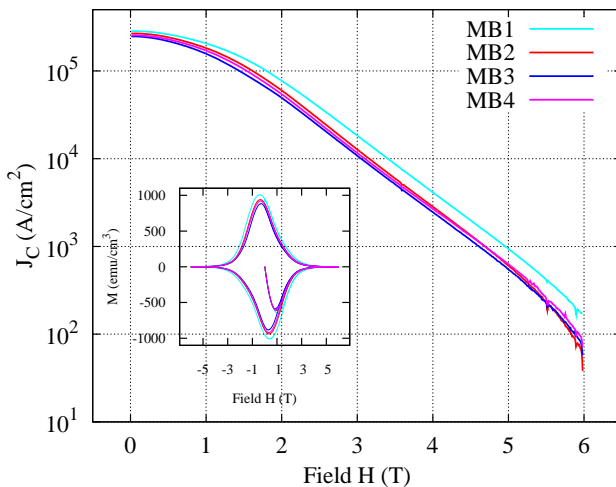


Figure 3.23: Magnetic  $J_C(H)$  plots at 15 K for the samples MB1, MB2, MB3 and MB4 heated at 850 °C/2h. Inset of the figure shows the corresponding M-H curves of the samples at 15 K.

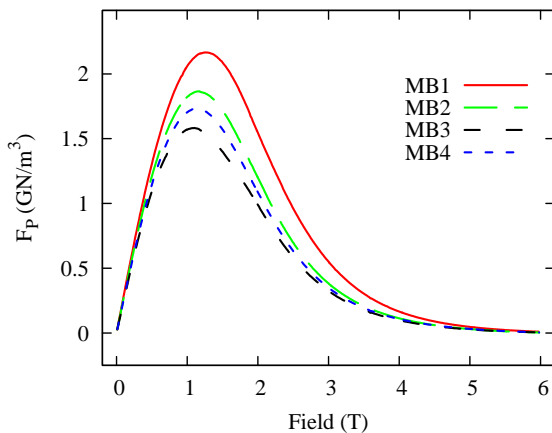


Figure 3.24: Field dependence of flux pinning force density for the samples MB1, MB2, MB3 and MB4



Figure 3.23 shows the  $J_C$  at 15 K in applied fields, estimated from the isothermal M-H curves by using the Bean model. Inset of the figure shows the corresponding M-H curves at 15 K for the samples. The sample MB1 has the best  $J_C$  value among all the samples upto the maximum field (6 T) studied. At high fields the  $J_C$  of MB2, MB3 and MB4 are comparable but distinctly lower than that of MB1.

The flux pinning force density  $F_P$  ( $F_P = J_C \times B$ ) as a function of applied field for the samples is shown in figure 3.24. The sample MB1 clearly show enhanced flux pinning compared to the others. The flux pinning behaviour of all other samples is almost same. For the sample MB1 both  $F_{P_{max}}$  and the field for  $F_{P_{max}}$  are higher, implying increased number and strength of pinning centers in the sample.

### 3.2.4 Discussion of the results

The results of above studies indicates :

1. As the sintering temperature and its duration increase the amount of crystalline MgB<sub>2</sub> increases.
2. The average grain size of crystalline MgB<sub>2</sub> increases with increasing the sintering temperature and durations.
3. The critical temperature of the MgB<sub>2</sub> remains almost same for samples prepared at different temperatures, while  $J_C(H)$  is slightly higher for samples prepared at relatively lower temperatures.
4. The reactivity of Mg with B is better for smaller sized Mg particles. A considerable amount of Mg left unreacted in samples prepared from larger sized Mg powders.
5. The critical temperature of MgB<sub>2</sub> is almost unaffected by the Mg size variation, but the critical current density is affected.  $J_C(H)$  and flux pinning strength were higher for samples synthesized with lower sized Mg particles and lower for samples synthesized with higher sized Mg particles.

The observed results can be explained as follows. The reaction mixture is considered as a homogeneous mixture of Mg and B powders. Mg melts at  $\sim 650$  °C and the melting temperature of B is higher than 2000 °C.

Detailed kinetic analysis for the Mg + B system shows that  $\text{MgB}_2$  phase starts to form much below the melting of Mg ( $< 650\text{ }^\circ\text{C}$ ) [159–161]. At these temperatures, solid-solid diffusion of Mg and B particles takes place and the  $\text{MgB}_2$  phase starts to form at a slow rate. The reaction between Mg and B powders starts at the Mg-B interface and a layer of  $\text{MgB}_2$  forms at the interface [159–161]. Once the temperature reaches the melting point of Mg ( $\sim 650\text{ }^\circ\text{C}$ ), Mg melts and then liquid-solid reaction takes place, through diffusion. At the reaction temperature Mg melts but remains as globules and can be considered as particles in liquid phase. The formation of  $\text{MgB}_2$  generates heat, further promotes the melting and reaction of Mg with B. The reaction between Mg and B starts at Mg-B interface and the particles diffuse further across the formed  $\text{MgB}_2$  layer, and the reaction grows around the layer [159–161], until the growth is pinned (mainly by pores). The rate of diffusion depends on the temperature and more particles diffuse with increased sintering temperature and durations.

At lower temperatures and durations the rate of diffusion is low and is the reason for the observed unreacted Mg in these samples sintered at lower temperatures and durations. At much higher temperatures the vapor pressure of Mg is high and a great deal of liquid Mg turns into Mg vapor, leading to a vapor-solid interaction. At higher sintering temperatures the diffusion rate is higher which improves the grain growth, resulting  $\text{MgB}_2$  crystals of increased grain sizes.

As the  $\text{MgB}_2$  grain grows at the Mg-B interface, diffusion rate decreases with increase in the thickness of the interfacial  $\text{MgB}_2$  layer. The reaction kinetics of *in situ*  $\text{MgB}_2$  discussed by Cui *et al* [162] also suggests that the rate of reaction is most likely to be inversely proportional to the thickness of the  $\text{MgB}_2$  layer formed between the reactants. For Mg particles of size smaller or comparable with B, the Mg-B interface will be sufficient to diffuse and react the Mg and B particles completely. For Mg particles of size much higher compared to B particles, some Mg will remain unreacted and this will be trapped inside the  $\text{MgB}_2$  layers as inclusions since all the Mg inside may not diffuse as the diffusion rate decreases with growth of interfacial  $\text{MgB}_2$ . Thus the reaction between Mg and B practically ceases locally after a certain period since diffusion rate approaches zero. In the SEM images of samples (figure 3.20) synthesized with higher sized Mg powders a lot of separated (not well connected)  $\text{MgB}_2$  grains can be seen. This may be due to the ceasing of local grain growth. But in samples synthesized with smaller sized Mg powders, the grains are comparably well

connected and the microstructure is more homogeneous. As no MgB<sub>4</sub> or other higher borides are detected in the samples, due to the incomplete reaction, small quantity of B can be at the grain boundaries as an amorphous impurity. For smaller starting Mg powders the MgB<sub>2</sub> grains formed will be also small, since Mg is the nucleation site and the reaction grows along the Mg-B interface. SEM images of the samples show that the grain size is lower for samples synthesized from smaller sized Mg powders, which is further supported by the FWHM results.

Grain boundaries are good flux pinning centers in MgB<sub>2</sub> [61, 122–124] and flux pinning improves with reduced grain size [125]. This is why samples with lower sized grains showed higher  $J_C(H)$  values.

### 3.3 Summary and conclusion

Bulk MgB<sub>2</sub> superconductor was prepared by a simple a Powder-In-Sealed Tube (PIST) method. In this method, Mg and B powders were sealed inside stainless steel tubes and heat treated in air, ie without any inert or vacuum atmosphere. The MgB<sub>2</sub> prepared by PIST method has good phase purity and superconducting properties. Only a trace amount of MgO is observed as an impurity in typical PIST sample and the sample has  $T_C$  38-39 K with a  $\Delta T_C \sim 1$  K and  $J_C$  of  $10^5$ - $10^6$  A/cm<sup>2</sup> at 5 K.

Influence of heat treatment temperature, duration and size of starting Mg powder on the microstructural and superconducting properties of *in situ* MgB<sub>2</sub> were studied for optimizing the preparation conditions. Reactivity of Mg with B decreases significantly due to the reduction in diffusion of particles across MgB<sub>2</sub> layer and the residual Mg increases with increase in the size of the starting Mg powder. MgB<sub>2</sub> prepared using Mg powder of size smaller or comparable with B powder has no/lesser residual Mg, and show better  $J_C$  in applied fields compared to other samples. Based of the phase analysis, crystalline and microstructure analyses and evaluation of superconducting properties, a sintering temperature of 800-850 °C for 2 hours is found to be the optimum for PIST method. Considering the availability and the observed good results Mg particles of size 25-53  $\mu\text{m}$  is selected for the further studies in the present work.



## Chapter 4

# Preparation and characterization of $\text{MgB}_2$ wires and tapes

This chapter describes the preparation and characterization of  $\text{MgB}_2$  superconductor in mono and multifilamentary wire and tape geometries. Over the years many techniques were developed for making LTS and HTS materials into wires and tapes. Of these, Powder-In-Tube (PIT) method is an easy and scalable method for large scale production of long length conductors. For  $\text{MgB}_2$  also PIT is the most preferred for long length fabrication. In the present study also chose *in situ* PIT method for the preparation of  $\text{MgB}_2$  wires and tapes as the method is most efficient for large scale industrial production of long length conductors.

In PIT method, the precursor powder is filled into suitable metallic tubes, mechanically rolled/extruded/drawn into desired size and shape followed by a heat treatment. In the case of  $\text{MgB}_2$ , the metallic sheath chosen must be chemically compatible with  $\text{MgB}_2$  and should not degrade the superconductivity. It must be non-reactive with Mg, B and  $\text{MgB}_2$ . The sheath metal must have adequate strength to give mechanical support to the brittle superconducting core, but also must be ductile enough to withstand the mechanical working. The metal sheath has to play a role of diffusion barrier for the volatile and reactive Mg. Several sheath materials such as Cu, Ag, Ni, Nb, Ti, Fe and some alloys like SS, monel (Cu-Ni) are tried for

MgB<sub>2</sub>. Of these most of the sheath materials form intermetallics or solid solutions with Mg/B, affecting the superconducting properties of the system to different extents depending on the reactivity [60].

In order to select a suitable sheath material, we carried out a systematic study of the reactivity of the commonly available sheath materials such as Fe, SS, Cu, Ag, Ni and Ta by mixing their fine powders with stoichiometric Mg and B and heat-treating the reaction mixtures at different temperatures. The studies showed that among the above metals only Fe, SS and Ta are acceptable for use as sheath materials for MgB<sub>2</sub> wire/tape fabrication. In the present work MgB<sub>2</sub> based wires and tapes were fabricated in both mono and multifilamentary geometries using Fe as the sheath material.

## 4.1 Reactivity of sheath materials with Mg/B

### 4.1.1 Experimental Details

The samples for reactivity study were prepared by *in situ* Powder-In-Sealed-Tube (PIST) method as detailed in chapter 3. Commercially available seamless stainless steel (SUS 304) tubes of 10 cm length with an outside diameter (OD) of 10 mm and inside diameter (ID) of 8 mm were used for the study. Stoichiometrically weighed and uniformly mixed Mg powder and amorphous B powder, added with a 10 wt.% sheath material powder viz. Ag, Cu, Fe, Ni, SS and Ta (99% purity, -200 mesh) were packed into the tubes, compacted mechanically and end-sealed by arc welding. Thirty such samples (five each with six different sheath material powders) were prepared and each set was subjected to heat treatment at 600 °C, 675 °C, 750 °C, 825 °C and 900 °C for 2 hours.

### 4.1.2 Characterizations

The phase analysis of the samples were performed by using powder XRD. Phase identification of the samples were performed using X'pert Highscore Software in support with ICDD-PDF-2 database. Quantitative phase analysis of the samples were carried out from the XRD. Microstructural examination and elemental analysis of the samples were done by using a scanning electron microscope (SEM-JEOL JSM 5600LV) equipped with an X-ray energy dispersive spectrometer (EDS).

### 4.1.3 Results and discussion

Figure 4.1 shows XRD patterns of the various sheath material viz. Ag, Cu, Fe, Ni, SS and Ta added samples heat treated at different temperatures viz. 600, 675, 750, 825, 900 °C for 2 h. The XRD measurements were performed on the ground cores, taken out by mechanically peeling off the SS sheath. From all the XRD patterns, it can be seen that MgB<sub>2</sub> formation is almost complete in all samples at around 825 °C and small peaks corresponding to MgO are also present.

For the Ag added sample (figure 4.1 a), reaction between Mg and Ag starts even at the temperatures of 600 °C. At 600 °C reaction between Mg and Ag forms an intermetallic Ag<sub>0.24</sub>Mg<sub>0.76</sub>, and after 750 °C, the Ag<sub>0.24</sub>Mg<sub>0.76</sub> fully converts into MgAg, reducing the effective superconductor volume. Above 750 °C the amount of MgAg phase is considerable and some of the peaks are very strong and sharp. The presence of Ag-Mg phases strongly impede the flow of super-currents from grain to grain, causing a decrease of current carrying capacity of the system [60].

For the Cu added sample (figure 4.1 b), the competition in reaction among Mg, Cu and B led to different phase formations. Significant Mg-Cu reaction took place even at 600 °C resulting in the formation of the binary phase Mg<sub>2</sub>Cu. As the reaction temperature is increased above 750 °C, Mg<sub>2</sub>Cu undergoes partial decomposition and releases a part of the Mg and this results in a phase composition of MgCu<sub>2</sub>. Thermodynamically, the Gibb's free energy of MgCu<sub>2</sub> is lower than that of Mg<sub>2</sub>Cu and this explains the formation of MgCu<sub>2</sub> which is more stable at higher reaction temperatures. There were reports on the deleterious effects of MgCu<sub>2</sub> formation in Cu sheathed conductors at temperatures above 750 °C [163–165]. These reactive phases both Mg<sub>2</sub>Cu and MgCu<sub>2</sub> act as obstacles to the supercurrent flow, creating weak links among MgB<sub>2</sub> grains.

For the Fe introduced sample, Fe remains inert towards both Mg and B at temperatures up to 825 °C (figure 4.1 c). For the 900 °C heat treated sample, the intermetallic compound Fe<sub>2</sub>B begins to form due to reaction of Fe with boron. Being highly brittle in nature Fe<sub>2</sub>B worsens the mechanical and conduction properties of the superconductor. Studies by Grovenor *et al* [166] showed the formation of Fe<sub>2</sub>B at temperatures in excess of 850 °C. However, the best  $J_C$  for MgB<sub>2</sub> wires are generally obtained with Fe as the

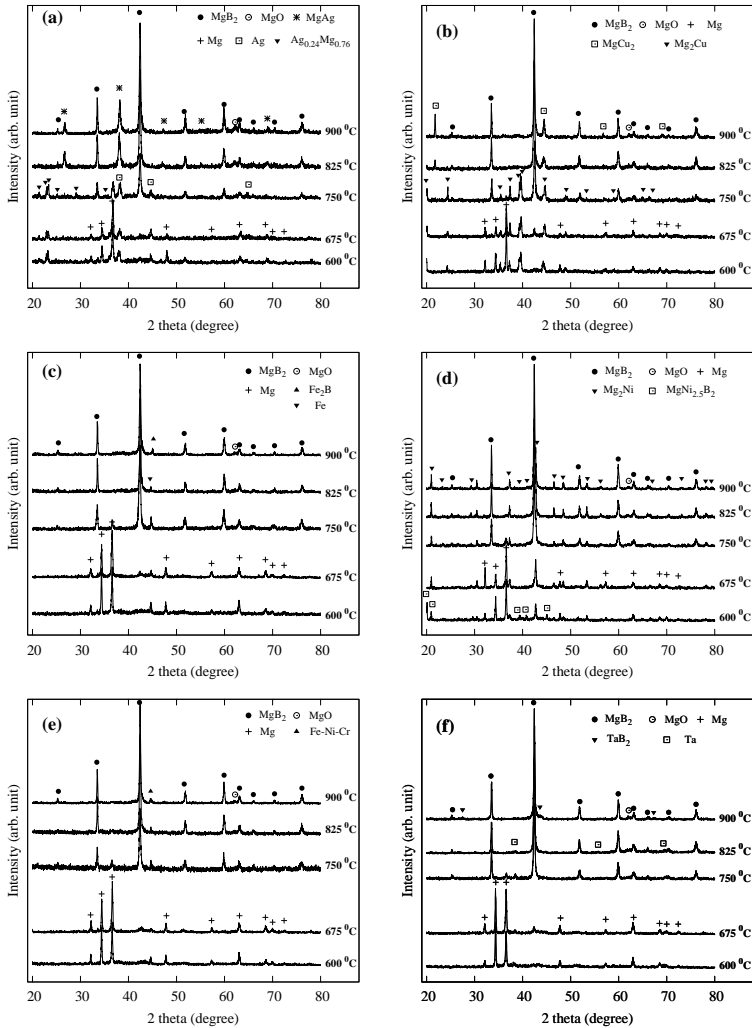


Figure 4.1: Powder XRD pattern of sheath material viz. (a) Ag, (b) Cu, (c) Fe, (d) Ni, (e) SS and (f) Ta added samples heat treated at different temperatures.

sheath material [167, 168], for relatively low temperature ( $< 850$  °C) heat treated wires/tapes wherein the reaction between Fe and  $\text{Mg/B}$  is minimal.



Ni added samples showed significant reaction at temperatures as low as 600 °C causing the formation of Mg<sub>2</sub>Ni (figure 4.1 d). At higher temperatures, boron also take part in the reaction process resulting in the formation of the tertiary compound MgNi<sub>2.5</sub>B<sub>2</sub> in large quantities. Bellingeri *et al* [169] observed a thick reaction layer of MgNi<sub>2.5</sub>Bi<sub>2</sub> by neutron diffraction at the Ni-MgB<sub>2</sub> interface while fabricating monofilamentary tapes.

Mg and B are found to be exceptionally inert with respect to stainless steel even up to the highest heat treatment temperature of 900 °C (figure 4.1 e), suggesting the chemical compatibility of SS for MgB<sub>2</sub> wire fabrication. It may be recalled that SS tubes were used for preparing all the samples in this study. However, not even a trace of any reacted phase is observed in any of the samples under the extreme heat treatment conditions used. No chemical reactions have been observed for the Ta introduced *in situ* processed samples upto a temperature of 825 °C (figure 4.1 f). At higher temperatures, Ta begins to react with B forming TaB<sub>2</sub> inside the core. The results of reactivity of *in situ* processed MgB<sub>2</sub> with various sheath materials at different temperatures are summarized in Table 4.1.

Table 4.1: Reaction products of Mg/B with various sheath materials.

Sheath material	Heat treatment temperature				
	600 °C	675 °C	750 °C	825 °C	900 °C
Ag	Ag <sub>0.24</sub> Mg <sub>0.76</sub>	Ag <sub>0.24</sub> Mg <sub>0.76</sub>	Ag <sub>0.24</sub> Mg <sub>0.76</sub>	MgAg	MgAg
Cu	Mg <sub>2</sub> Cu	Mg <sub>2</sub> Cu	Mg <sub>2</sub> Cu	MgCu <sub>2</sub>	MgCu <sub>2</sub>
Ni	Mg <sub>2</sub> Ni, MgNi <sub>2.5</sub> Bi <sub>2</sub>	MgNi <sub>2.5</sub> Bi <sub>2</sub>	MgNi <sub>2.5</sub> Bi <sub>2</sub>	MgNi <sub>2.5</sub> Bi <sub>2</sub>	MgNi <sub>2.5</sub> Bi <sub>2</sub>
Fe	No reaction	No reaction	No reaction	No reaction	Fe <sub>2</sub> B
SS	No reaction	No reaction	No reaction	No reaction	No reaction
Ta	No reaction	No reaction	No reaction	No reaction	TaB <sub>2</sub>

Figure 4.2 depicts the formation profile of the various phases formed in the reaction mixture with different sheath material powders during the *in situ* processing of MgB<sub>2</sub> heat treated at different temperatures. ‘Other phases’ labeled in the figure refers to all phases other than MgB<sub>2</sub> present in the samples and ‘reactive phase’ refers to compounds of sheath material with Mg and B. In all the cases formation of MgB<sub>2</sub> starts at 600 °C and the reaction rate attains a maximum in the temperature range from 675

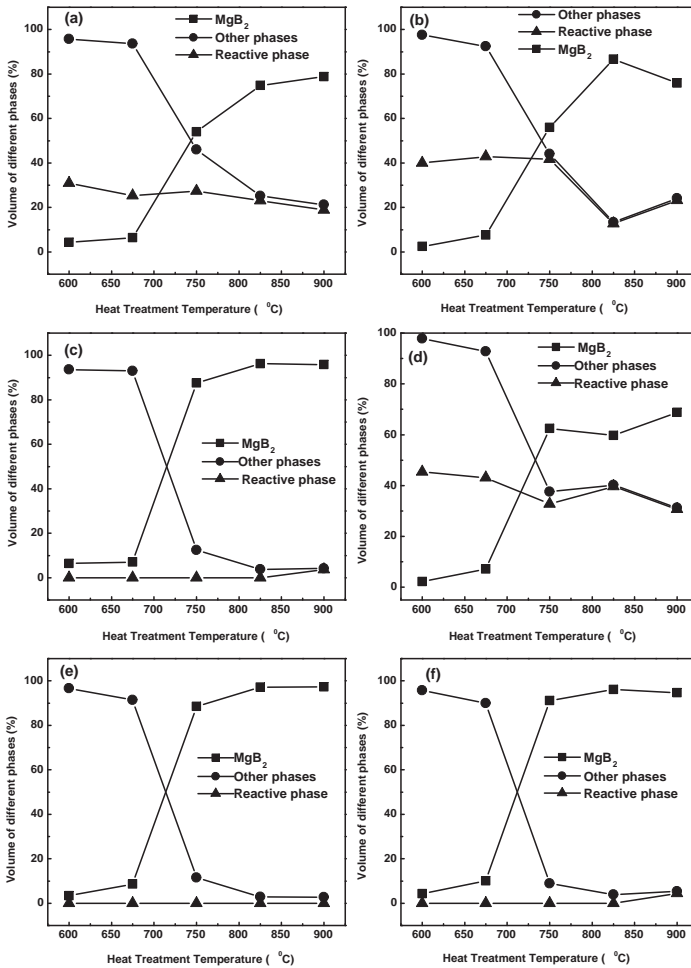


Figure 4.2: Quantitative values of the various phases formed in the sheath material (a) Ag, (b) Cu, (c) Fe, (d) Ni, (e) SS and (f) Ta introduced *in situ* processed  $MgB_2$  at different temperatures.

to 750 °C irrespective of the added sheath material powder. For Fe, SS and Ta the  $MgB_2$  formation curves are almost identical (figure 4.2 c, e and

f) yielding high purity  $\text{MgB}_2$  (Vol.% of 96.2, 97.2 and 96.1 respectively) at a temperature of 825 °C with little or no reacted phases. Beyond this temperature the rate of  $\text{MgB}_2$  formation stagnates without any significant deterioration in purity upto 900 °C. But Ag, Cu and Ni added samples show (figure 4.2 a, b and d) markedly larger amount of reactive phases, considerably reducing the relative amount of  $\text{MgB}_2$  phase in the core to 78.8%, 86.8% and 68.8% respectively within the temperature 900 °C. Of these, volume % of  $\text{MgB}_2$  is lowest for the Ni added samples. The much higher reactivity of Ag, Cu and Ni make them unsuitable for the fabrication of  $\text{MgB}_2$  based conductors even at lower temperatures.

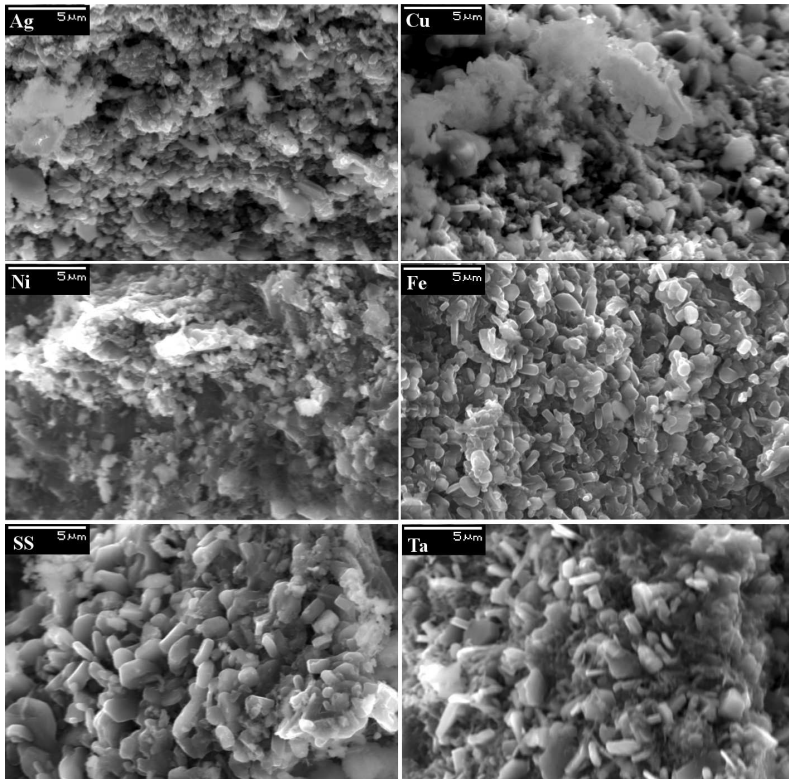


Figure 4.3: SEM images of the sheath material viz. Ag, Cu, Fe, Ni, SS and Ta added samples heat treated at 900 °C/2h.

Figure 4.3 shows the scanning electron micrographs (SEM) of various sheath material introduced *in situ* processed  $\text{MgB}_2$  samples heat treated at  $900^\circ\text{C}/2\text{h}$ . Typical hexagonal grains of  $\text{MgB}_2$  can be observed in all the microstructures. However, larger quantities of fine grained precipitates of the reacted products are observed for Ag, Cu and Ni added samples, showing their extensive reaction with Mg and/or B. In order to find out the atomic composition of the reacted phases energy dispersive X-ray (EDX) analysis was carried out. Figure 4.4 shows typical energy dispersive spectra (EDS) of the precipitated areas of Ag and Cu added *in situ* processed  $\text{MgB}_2$  samples. The EDX microanalysis has revealed that the precipitated area of Ag added sample has an approximate atomic composition Mg : Ag of 1:1 ( $\text{MgAg}$ ) and for Cu added sample, it has a composition Mg:Cu of 1:2 ( $\text{MgCu}_2$ ). These observations are consistent with the X-ray diffraction studies.

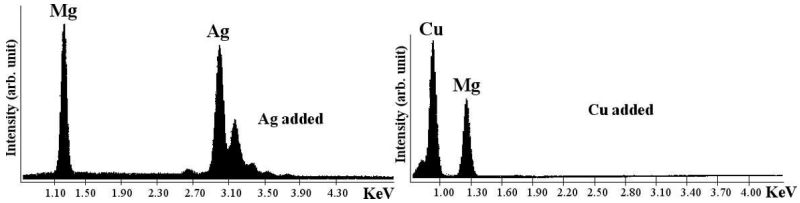


Figure 4.4: Energy dispersive spectra (EDS) of the reactive phase formed in Ag and Cu added samples heat treated at  $900^\circ\text{C}/2\text{h}$ .

For an *in situ* conductor fabrication method, the sheath material plays a very crucial role in determining the superconducting properties of  $\text{MgB}_2$  conductors. Conductors with better properties could be achieved if we use the right sheath material which should be primarily non-reactive with Mg/B at heat treatment temperatures. The present study shows that Ag, Cu and Ni undergo markedly higher reaction during the *in situ* processing of  $\text{MgB}_2$ , which make them unsuitable for conductor fabrication. On the other hand, SS, Fe and Ta show no or very little reaction at the heat treatment temperatures and hence these can be considered as potential candidates for  $\text{MgB}_2$  wire manufacturing. However, factors such as limited mechanical workability of SS and high cost of Ta make Fe, the best choice as the sheath material for *in situ*  $\text{MgB}_2$  wire/tape fabrication.

## 4.2 Influence of sheath material reactivity on superconducting properties of MgB<sub>2</sub>

### 4.2.1 Experimental Details

Based on the above study of the reactivity of various sheath materials with Mg/B, four samples, added with Fe, SS, Cu and Ni, (10 wt.% of each) and heat treated in air at 825 °C for 2 hours were selected for superconducting property measurements. Here after the samples added with SS, Fe, Cu and Ni are named as MBSS, MBFe, MBCu and MBNi respectively. The superconducting magnetic measurements were carried out by a vibrating sample magnetometer in Physical Property Measuring System (PPMS), Quantum Design, USA on the rectangular shape of samples having sizes of 3mm × 3mm × 1.5mm.

### 4.2.2 Results and discussions

The XRD patterns of the samples are shown in different plots in figure 4.1. However for the sake of comparison, the XRD patterns of samples added with SS, Fe, Cu and Ni sheath powders and heat treated at 825 °C for 2h are shown in figure 4.5. All X-ray diffraction results give sharp peaks of MgB<sub>2</sub> phase with only a minute fraction of MgO. The impurity phases formed are marked in the figure. Lattice parameter calculations show that there is no significant variation in lattice parameters  $a$  or  $c$  of MgB<sub>2</sub> (table 4.2) within the experimental limit. This indicates that the added sheath materials are not substituted at either Mg or B sites in MgB<sub>2</sub>. The lattice parameters  $a$  and  $c$ , Vol.% of MgB<sub>2</sub> phase,  $T_C$ ,  $H_{irr}$  and  $J_C$  data for MBSS, MBFe, MBCu and MBNi samples obtained from this work are summarized in table 4.2.

Figure 4.6 illustrates the DC magnetization versus temperature (M-T) plots in zero field cooled (ZFC) condition under an applied field of 20 Oe for SS, Fe, Cu and Ni added MgB<sub>2</sub> samples. The ZFC branch of the magnetization undergoes a diamagnetic transition in the range 37.8-38.5 K. Fe added sample shows relatively higher  $T_C$  (38.5 K) while  $T_C$  of MBSS (38.2 K) and MBCu (38.3 K) are almost same and that of MBNi sample is slightly lower (37.8 K). The lower  $T_C$  of Ni added sample may be due to the reduction of superconducting volume (60% MgB<sub>2</sub>) which is cleared from quantitative phase analysis of XRD data, as shown in table 4.2. The samples MBSS and MBFe exhibit positive magnetization above transition

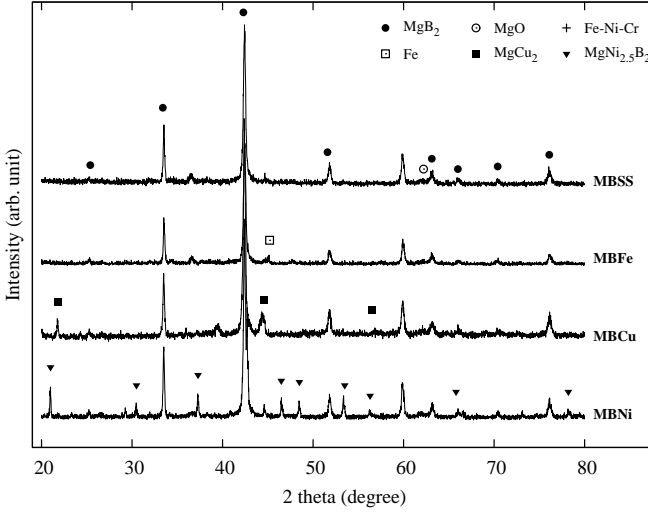


Figure 4.5: X-ray diffraction patterns for MgB<sub>2</sub> samples added with 10 wt.% of sheath powder SS, Fe, Cu and Ni and heat treated at 825 °C/2h.

temperature, likely due to the paramagnetic or ferromagnetic nature of additives. Although Ni is ferromagnetic below its curie temperature, Ni added MgB<sub>2</sub> sample does not show any positive magnetization above  $T_C$  since the Ni powder reacted with Mg and B forming MgNi<sub>2.5</sub>Bi<sub>2</sub>.

Table 4.2: Structural and superconducting characteristics of MgB<sub>2</sub> samples added with sheath materials.  $J_C$  and  $H_{irr}$  values are at 5 K

Sample	$a$ (Å)	$c$ (Å)	Vol. of MgB <sub>2</sub> (%)	$T_C$ (K)	$J_C$ at 2 T (A/cm <sup>2</sup> ) ( $\times 10^4$ )	$J_C$ at 5 T (A/cm <sup>2</sup> ) ( $\times 10^3$ )	$H_{irr}$ (T)
MBFe	3.086	3.525	97.2	38.2	11.8	6.8	7.8
MBSS	3.089	3.523	96.2	38.5	8.5	5.2	7.7
MBCu	3.084	3.526	86.6	38.3	5.2	2.9	7.1
MBNi	3.086	3.525	60.0	37.8	4.5	2.0	6.9

The field dependent magnetization of MgB<sub>2</sub> samples added with sheath powders SS, Fe, Cu and Ni is shown in figure 4.7. It appears that the first

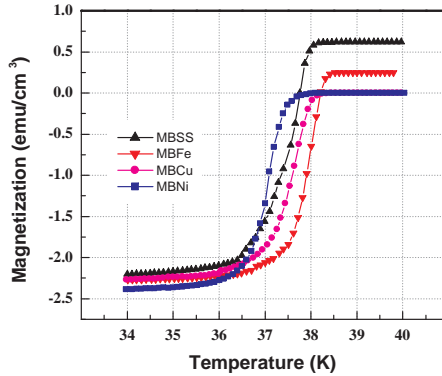


Figure 4.6: M-T plots in zero field cooled (ZFC) condition at 20 Oe for MBSS, MBFe, MBCu and MBNi.

and third quadrants and the second and fourth quadrants are replica to each other. The magnetic hysteresis loop widths of MBSS and MBFe are larger than those of MBNi and MBCu showing the former's higher magnetization under external magnetic field. Samples MBFe and MBSS show slight paramagnetic shift due to the presence of paramagnetic components such as Fe and SS powders.

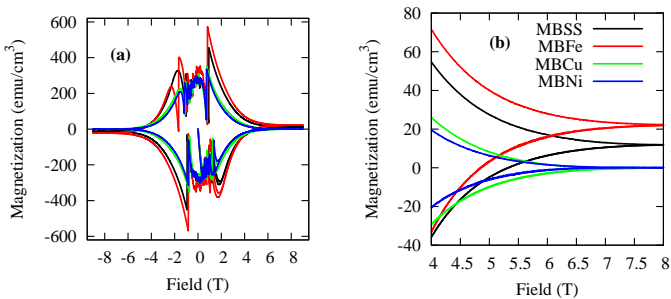


Figure 4.7: (a) M-H plots (at 5 K) of MgB<sub>2</sub> samples added with sheath powders SS, Fe, Cu and Ni and (b) enlarged view at high fields.

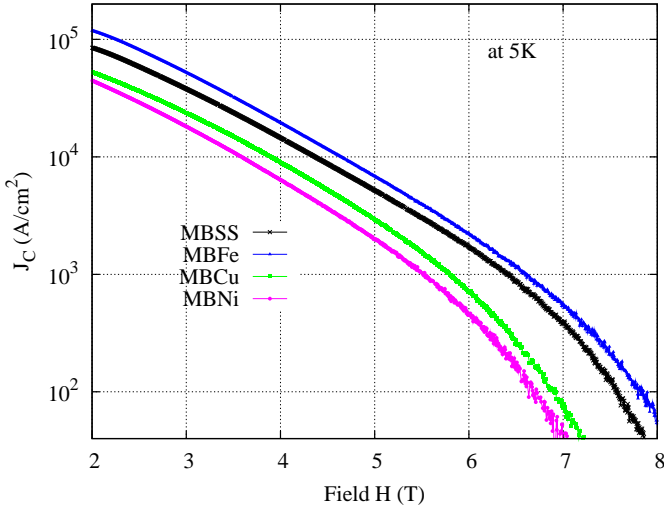


Figure 4.8:  $J_C(H)$  curves at 5 K of MgB<sub>2</sub> samples added with sheath powders SS, Fe, Cu and Ni.

The critical current density ( $J_C$ ) was estimated from the width of the M-H curves in applied fields ( $H$ ) at 5 K by using Bean model. Figure 4.8 shows the dependence of  $J_C$  with magnetic fields upto 8 T. As shown in the figure  $J_C(H)$  characteristics imply that the intragrain  $J_C$  of Fe added MgB<sub>2</sub> sample attains better values among all samples. The intragrain  $J_C$  values for MBFe sample are  $11.9 \times 10^4$  A/cm<sup>2</sup> at 2 T and  $6.8 \times 10^3$  A/cm<sup>2</sup> at 5 T whereas for MBSS sample  $J_C$  values at 2 T and 5 T are  $8.5 \times 10^4$  A/cm<sup>2</sup> and  $5.2 \times 10^3$  A/cm<sup>2</sup>, comparable to that of Fe added sample.  $J_C$  values of sample MBCu are  $5.2 \times 10^4$  A/cm<sup>2</sup> at 2 T and  $2.9 \times 10^3$  A/cm<sup>2</sup> at 5 T and those of MBNi are  $4.5 \times 10^4$  A/cm<sup>2</sup> at 2 T and  $2 \times 10^3$  A/cm<sup>2</sup> at 5 T. Enhanced  $J_C$  values of Fe and SS added samples show a direct correlation with their better phase purity comparing with Cu and Ni added samples. At higher fields MBSS and MBFe samples show two or three times larger  $J_C$  than the other samples containing reacted phases. The steep drop in  $J_C$  at higher fields (> 6 T) in all samples is attributed to the flux penetration into the grain boundaries that may contain impurities. The weaker grain connectivity and greater flux penetration due to the presence of impurities of reacted sheath powders in the grain boundaries lead to a larger reduction of  $J_C$  in MBCu and MBNi samples at higher fields.



The irreversibility field  $H_{\text{irr}}$ , defined as the field at which critical current  $J_C$  falls below 100 A/cm<sup>2</sup>, for all samples at 5 K is shown in table 4.2. For MBFe and MBSS  $H_{\text{irr}}$  values at 5 K are 7.8 T and 7.7 T while those of MBCu and MBNi are 7.1 T and 6.9 T respectively. Higher  $H_{\text{irr}}$  of Fe and SS added samples is attributed to the higher superconducting area, better microstructure and unreacted sheath powders in MgB<sub>2</sub> acting as grain boundary pinning centers. The reacted additives in Cu and Ni added samples reduce the superconducting area and weaken the grain connectivity without any enhancement in flux pinning, causing reduced  $J_C(H)$  and  $H_{\text{irr}}$  values.

From the results it is very clear that Fe is the most suitable material with respect to chemical inertness with Mg/B at the reaction temperature and retention of superconducting properties of the MgB<sub>2</sub> core. Fe is easily available and is relatively cheap. It has adequate hardness to give mechanical support to the brittle superconducting core. It has enough strength and ductility to withstand mechanical rolling. Fe sheath effectively acts as a diffusion barrier for the volatile and reactive Mg. Considering these facts we choose iron as the sheath material for MgB<sub>2</sub> conductor fabrication.

## 4.3 Preparation of MgB<sub>2</sub> conductors

Mono and multifilamentary MgB<sub>2</sub> wires and tapes were prepared by the *in situ* Powder-In-Tube (PIT) method. Figure 4.9 presents the preparation method of mono and multifilamentary MgB<sub>2</sub> wires and tapes.

### 4.3.1 Monofilamentary wires and tapes

Fe tubes of length 2.5-5 cm, outside diameter 4 mm and inside diameter 2 mm were used for the regular short length conductor fabrication. For long length conductors 5-10 cm long and OD/ID of 8/6 or 5/3 mm tubes were used. The tubes were filled with homogeneously mixed Mg and B powders and mechanically compacted. Brass studs were used as plugs to seal the ends of the tubes. The composite tubes were groove rolled down to desired dimensions without any intermediate annealing. The regular wires prepared had a diameter of 1.4-2.0 mm, while the minimum diameter for rolled wire was  $\sim 1.1$  mm. For the preparation of tapes these groove rolled wires were then flat rolled to the desired geometry, using a flat roller. Typical flat rolled tapes had dimensions  $3\text{-}4 \times 0.8\text{-}1.6$  mm (width  $\times$  thickness).

The ends of the wires and tapes were sealed by arc welding. These wires and tapes were then heat treated at 650-750 °C for 0.5-2 hours. Some of the wires/tapes were heat treated by electrical self-heating (described in section: 4.8) and others were heat treated in a muffle furnace. After heat treatment short length samples were cut for various characterizations.

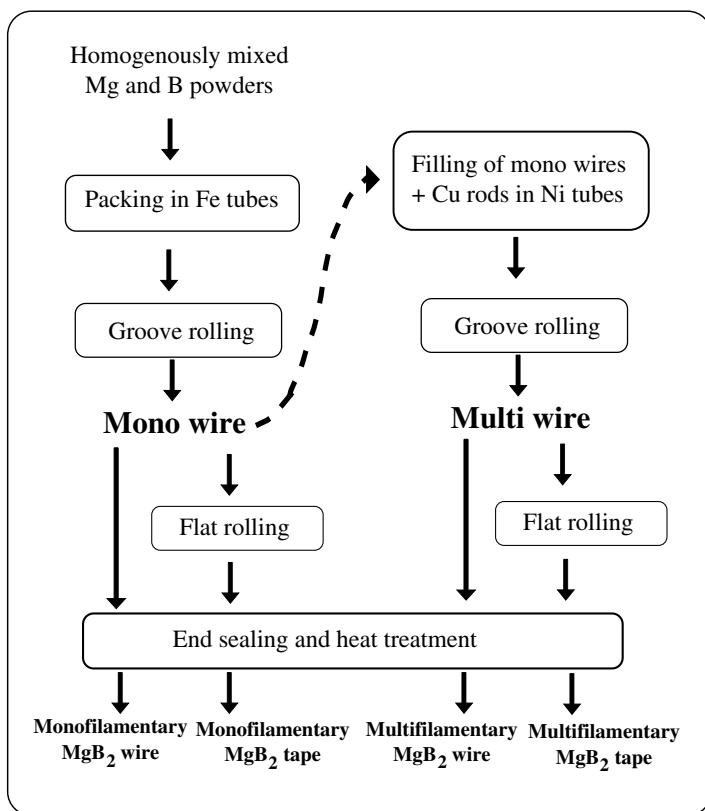


Figure 4.9: Flowsheet showing the preparation method of mono and multifilamentary  $\text{MgB}_2$  wires and tapes.

### 4.3.2 Multifilamentary wires and tapes

In a stabilized practical multifilamentary conductor, there has to be many filaments of sheathed  $\text{MgB}_2$  superconductor in a metallic matrix. A signifi-

cant area fraction of the multifilamentary conductor must contain a thermal stabilizer material:- metals with high thermal and electrical conductivities. During an accidental quench the stabilizer has to dissipate the heat generated in the conductor as fast as possible. The stabilizer also provides a parallel path to the current flow during the quench. In the present work we prepared multifilamentary MgB<sub>2</sub> conductors using Fe as inner sheath, Cu as stabilizer and Ni as outer sheath. Cu is used as the stabilizer, since it has high thermal and electrical conductivity and relatively low cost.<sup>1</sup> The outer sheath must have good mechanical properties to support the conductor and must be chemically stable with environment. We have considered stainless steel (SS), mild steel (MS), monel (an alloy of Cu and Ni) and Ni for the outer sheath material. Among these Ni is chosen as the outer sheath due to its high oxidation resistance at high temperature heat treatment and good mechanical properties.

To prepare multifilamentary wires the grove rolled monofilamentary wires (OD ~ 2-2.5 mm) were cut, bundled and packed inside Ni tubes of outside diameter 8 mm and inside diameter 6 mm. Cu wires of diameter 0.75-2 mm were also bundled inside the Ni tube along with the filaments. The composite was then then groove rolled for multifilamentary wires. For the preparation of tapes these groove rolled wires were then flat rolled to the desired geometry. The rolled wires and tapes were then heat treated as in the case of monofilamentary ones. The maximum length of the wire prepared is about 2 m and the maximum number of filaments in multifilamentary wires is 10. A typical wire has 1.5-2 mm outside diameter and a typical stabilized tape has the dimensions of ~ 1-2 mm thickness and 3-5 mm width and upto 10 superconducting filaments.

Figure 4.10 shows a schematic diagram of the filling and rolling processes for both mono and multifilamentary conductors and for both wire (groove rolling) and tape (flat rolling) rolling. For the rest of the thesis, the following short names are used to represent mono and multi filamentary wire and tape samples.

Mono (Single) filamentary Wire	SW
Mono (Single) filamentary Tape	ST
Multi filamentary Wire	MW
Multi filamentary Tape	MT

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<sup>1</sup>Silver (Ag) also has high thermal and electrical conductivity, but it is expensive.

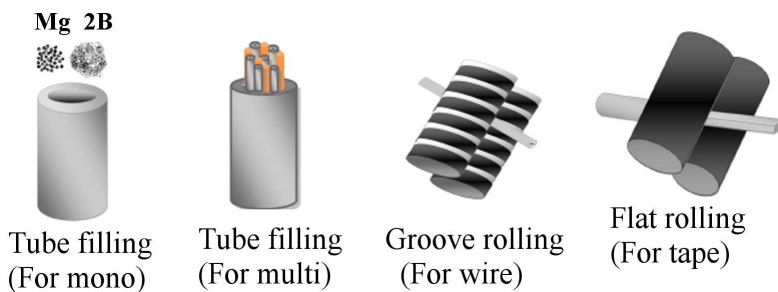


Figure 4.10: Schematic diagram of the filling and rolling processes for mono and multifilamentary conductors.

## 4.4 Problems faced during fabrication of conductors

Compared to the  $\text{MgB}_2$  bulk preparation, the wire and tape preparations were faced with a number of problems. The major problem faced during fabrication was the cracking of the sheath material. Even micro cracks proved costly because  $\text{MgO}$  content of such samples was very high which seriously affected the superconducting property. Figure 4.11 (a) shows a piece of wire which cracked during rolling. Figure 4.11 (b) shows the same region after the heat treatment. Here the crack is further developed and the  $\text{MgO}$  formed is seen as a white cloudy mass. For wires and tapes the surface cracking during rolling arises mainly due to work hardening and/or sheath thinning. By selecting tubes with proper wall thickness, optimizing the initial powder packing density and controlling the area reduction rate during rolling etc we could solve the sheath cracking problem completely. For tapes, in addition to the surface cracking, there was edge cracking also. This generally occurred during initial stages of flat rolling, where the cross section of the conductor starts to change from circular to rectangular. This problem also was solved by controlling the rolling parameters such as rolling speed and area reduction ratio per pass etc. For both wires and tapes the cracking tendency was higher for multifilamentary geometries. The problem of cracking was more in lower grooves.

In the case of multifilamentary conductors the ductility mismatch between Fe, Cu and Ni also caused rolling problems. These materials elongate differently during the initial stages of rolling. The initial non uniform

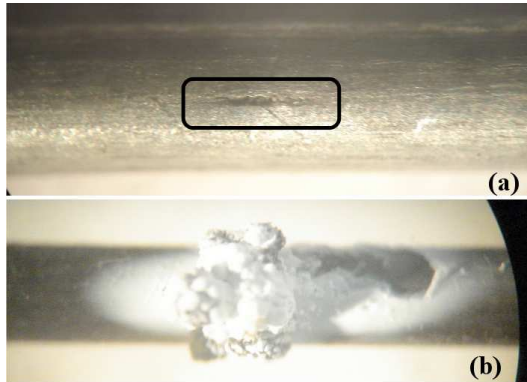


Figure 4.11: Photograph of (a) a macro scale crack on the surface of a rolled mono wire and (b) the same region after heat treatment (The photograph is taken on electrically self-heated sample). Here the crack is further developed and the MgO formed is seen as a white cloudy mass.

elongation results non uniform properties at both the ends, compared to the middle of the conductor. As the rolling progresses the diameter of the composite tube gets reduced and the whole composite elongates together. In order to account this, a portion of both ends of the rolled conductors were cut before heat treatment. The end sealing of conductors before heat treatment also raised some hurdles. Fe is easily weldable while Ni and Cu are not. A capping technique is used to perfectly seal the ends. In this, the ends of the conductors were inserted to suitable iron tubes of short length and mechanically fixed with the conductor and then ends of the iron tubes were welded. Figure 4.12 shows schematic illustrations of the problems as described above.

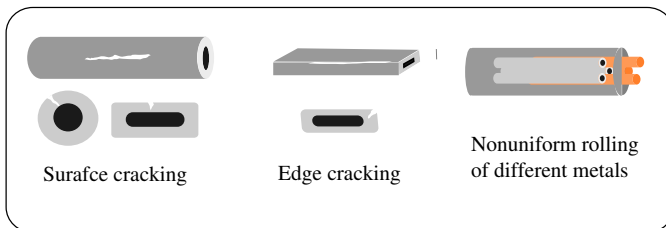


Figure 4.12: Schematic Illustrations of some of the problems faced during rolling.

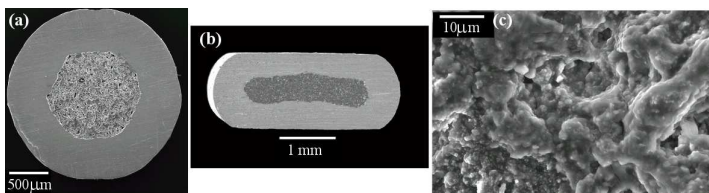


Figure 4.13: SEI SEM images of cross sections of (a) mono wire, (b) mono tape and (c) the core of mono wire.

## 4.5 Structural characteristics of $\text{MgB}_2$ conductors

Figure 4.13 shows the SEI SEM images of a mono filamentary wire (a) and tape (b). The images also show distinct and clear sheath and core as observed in the optical micrographs. Figure 4.13 (c) shows the enlarged view of the core of the wire. The image shows large pores in the core, characteristics of *in situ* synthesized  $\text{MgB}_2$ , caused due to the low green

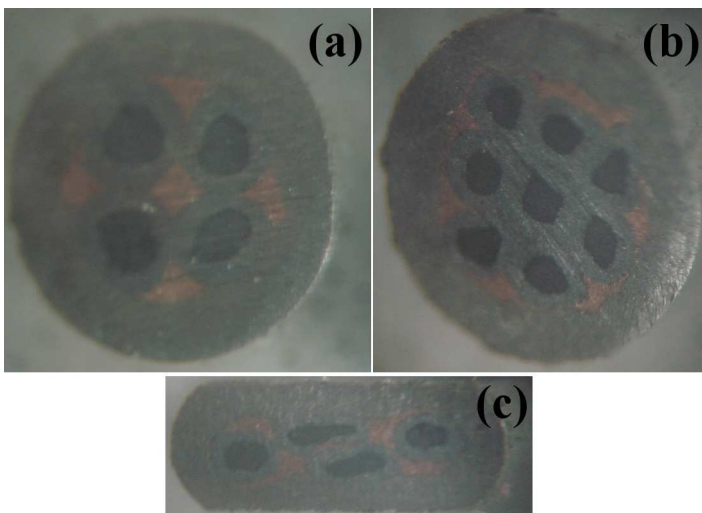


Figure 4.14: Optical micro graphs of multifilamentary  $\text{MgB}_2$  conductors (a) 4 filament wire (b) 8 filament wire and (c) 4 filament tape. Dimensions : OD = 2.1 mm for wires and cross section =  $4 \times 1 \text{ mm}^2$  for tape.

density of the mixtures and the volume shrinkage during  $\text{MgB}_2$  formation.

Figure 4.14 shows the optical micrographs of the cross sections of some of the monofilamentary and multi filamentary samples. The micrographs show the  $\text{MgB}_2$  core distinct and clear in both mono and multi. The outer sheath, superconducting core and the metallic matrix are clearly visible and distinguishable. The core-sheath interface is observed to be distinct, indicating the non-reactivity of the core with sheath metal. The Cu wires are also clearly visible without any significant diffusion between the different metals. No cracks or non uniformities were observed and the cross section of the wire and tape are almost circular and rectangular respectively in the micrographs.

Optical microscopy measurements, taken with the help of a scale built into the eyepiece, were used for the exact estimation of core and sheath cross sectional areas of mono/multi filamentary wires/tapes. For both mono wires and tapes,  $\text{MgB}_2$  core has  $\sim 25\%$  and the Fe sheath has  $\sim 75\%$  of the total cross sectional area respectively. The relative cross sectional area of  $\text{MgB}_2$  core for mono filamentary wire and tapes are shown in figure 4.15. For a typical multifilamentary conductor the cross sectional area  $\sim 10\%$  for  $\text{MgB}_2$  core,  $\sim 8\%$  for Cu,  $\sim 35\%$  for Fe and  $\sim 47\%$  for the outer Ni sheath.

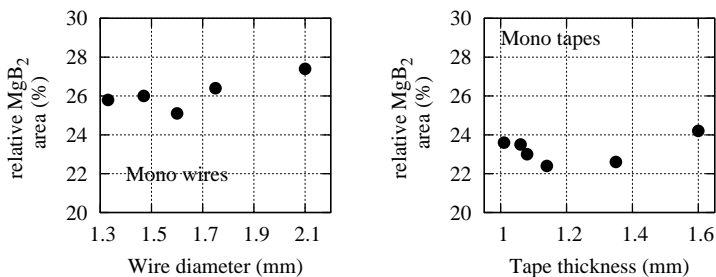


Figure 4.15: The cross sectional area of  $\text{MgB}_2$  core (in percentage) for mono filamentary wires and tapes for different diameter and thickness.

The powder XRD pattern of the ground  $\text{MgB}_2$  core of a monofilamentary wire is shown in figure 4.16, as a typical case. Crystalline  $\text{MgB}_2$  with minor amounts of  $\text{MgO}$  is observed in the samples. Unlike some of

the earlier reports no peaks of Fe containing phases such as  $\text{Fe}_x\text{B}$  phases are observed in the samples. This shows the non-reactivity of the sheath material with the Mg/B powders at the reaction temperature. The quality (crystallinity and phase purity) of  $\text{MgB}_2$  formed in the wire/tape is as good as that of  $\text{MgB}_2$  bulks prepared by PIST method as discussed in chapter 3. Calculated lattice parameters of the prepared  $\text{MgB}_2$  wires and tapes were consistent with the values observed for bulks.

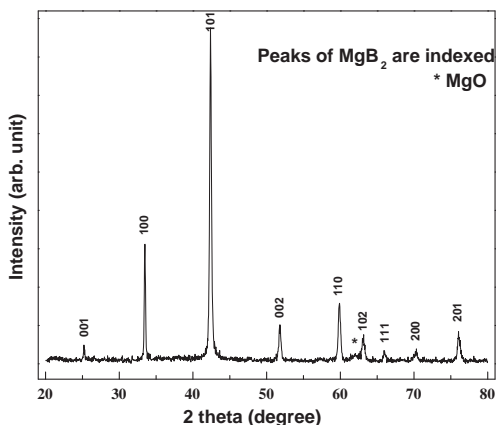


Figure 4.16: Powder XRD pattern of the ground  $\text{MgB}_2$  core of a monofilamentary wire.

## 4.6 Superconducting properties of $\text{MgB}_2$ conductors

Figure 4.17 and 4.18 show the resistance versus temperature plots of a mono and multifilamentary wire and tape samples. Inset of the figures show the enlarged plots near the transition region. Both mono and multi wire and tape have sharp transition at around 39 K. Mono filamentary conductors have a transition temperature ( $T_C$ ) in the range 38.2-39.0 K with transition width  $\Delta T_C < 1$  K. For multi filamentary conductors the  $T_C$  was in the range 38.0-38.5 K with transition width  $\Delta T_C < 1.5$  K. The almost



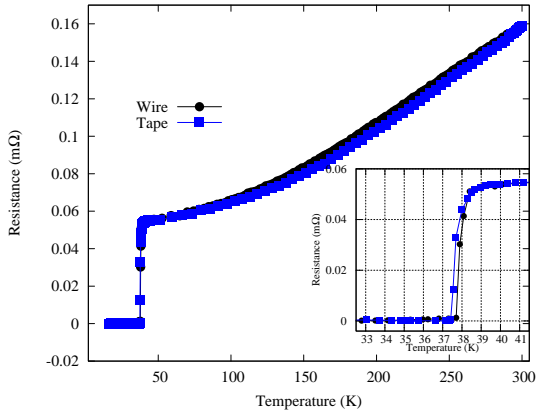


Figure 4.17: R-T plots of typical monofilamentary wire and tape. Inset of the figure shows zoomed view near the superconducting transition.

constant  $T_C$  and low  $\Delta T_C$  values of the wires/tapes as those observed in bulk samples indicate the good quality and homogeneity of the superconducting core in the wire/tape.

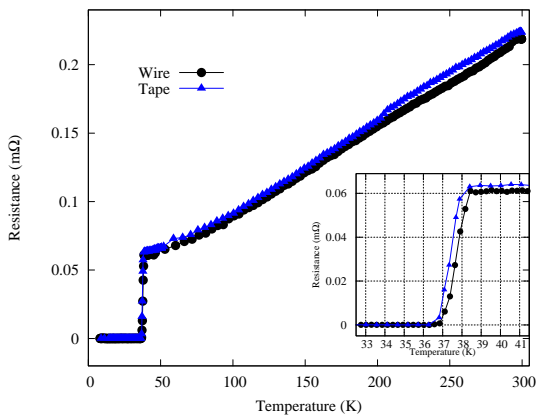


Figure 4.18: R-T plots of typical multifilamentary wire and tape. Inset of the figure shows zoomed view near the superconducting transition.

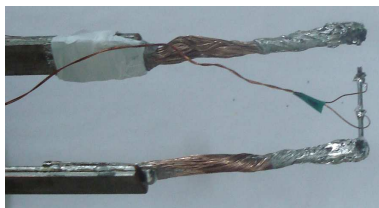


Figure 4.19: Photograph of a sample contact melted during high current transport measurement.

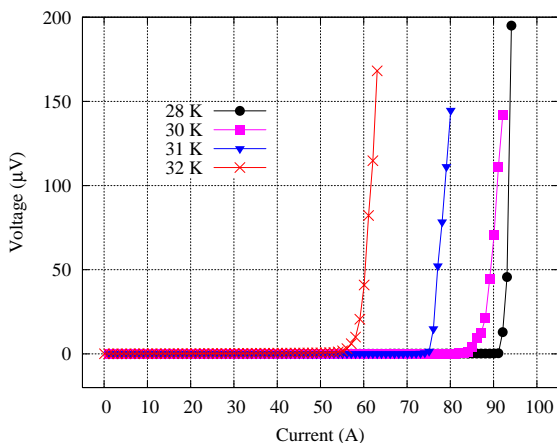


Figure 4.20: I-V plot of a typical monofilamentary  $\text{MgB}_2/\text{Fe}$  wire (1.33 mm diameter) at different temperature.

Another important task is to find the current carrying capability of the prepared conductors. The measurement of transport current properties of  $\text{MgB}_2$  conductor is difficult especially at high currents (in self-field). The rapid warming of the current contacts may cause a premature quench and subsequent burn out of the sample. In cases when very high currents are passed the contact, especially the solder joints melts. Figure 4.19 shows the photograph of such a sample where the contact is broken. The current contact melted while passing  $\sim 870$  A current through the sample (monofilamentary wire of OD  $\sim 1.33$  mm, length 3 cm) at 4.2 K and self-field. In the present study I-V measurements (cryocooler based) were done at relatively high temperatures to restrict the current to low values, other

wise the heat generated at the current leads and contacts make the transport measurements difficult in the conduction cooling system.<sup>2</sup>

Figure 4.20 shows the I-V characteristics of a monofilamentary MgB<sub>2</sub> wire at different temperatures. The sample had a length of 6.5 cm and  $\sim 1.33$  mm diameter. The wire had a MgB<sub>2</sub> core of  $\sim 0.68$  diameter. The sample was heat treated at 650 °C for 1 hour. The I-V measurement is done at 28, 30, 31 and 32 K using a closed cycle cryostat, where the sample is cooled by conduction. Current is passed through the sample for few seconds and the corresponding voltage drop across a tap of gap 2 cm is noted and then the current was switched off for few seconds to remove the heat generated in the current leads. The wire showed a critical current of  $\sim 91$  A at 28 K, 85 A at 30 K, 75 A at 31 K and 56 A at 32 K respectively. Table 4.3 shows the corresponding critical current density and engineering current density for the sample. The sample have a engineering current density of more than  $10^3$  Acm<sup>-2</sup> and critical current density of more than  $10^4$  Acm<sup>-2</sup> at a temperature around 30 K.

Table 4.3: Critical current characteristics of the sample for the I-V plot shown in figure 4.20

Temperature (K)	$I_C$ (A)	$J_E$ ( $\times 10^3$ Acm <sup>-2</sup> )	$J_C$ ( $\times 10^4$ Acm <sup>-2</sup> )
28	91	6.5	2.5
30	85	6.1	2.3
31	75	5.4	2.1
32	57	4.0	1.5

Figure 4.21 shows the I-V characteristics of selected multi filamentary wires and tapes at 30 K. The corresponding engineering and critical current densities are tabulated in the inset of the figure. The wires have 1.6 mm diameter and 5 (for MW1) and 8 (for MW2) superconducting filaments. The tapes measured have cross sections  $3.2 \times 1.0$  and  $2.6 \times 1.1$  (in mm)

<sup>2</sup>During the undesirable quench the measured parameters may not be the intrinsic property of the conductor. It has also been suggested that some of the high  $n$  (sharp transitions) values measured arise due to the heating during the I-V measurement, rather than the intrinsic value [170]. In order to avoid these difficulties it is a general practice to measure the transport properties at relatively higher temperatures or higher applied fields [171–174].

and 4 superconducting filaments. Sample MW1 has a sharp transition at around 96 A, while the 8 filament multifilamentary wire of same OD has a less sharp transition at around 80 A. The tape samples have relatively lower  $I_C$  and  $J_C$  values compared to the wire samples.

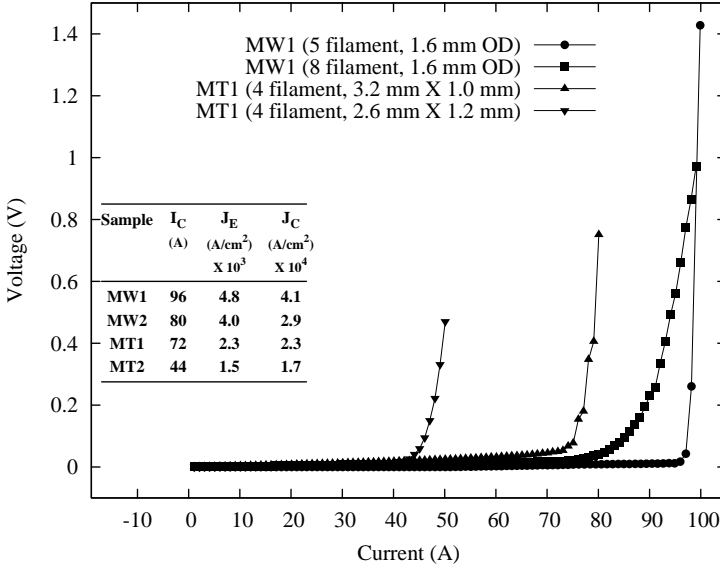


Figure 4.21: I-V plot of typical multifilamentary MgB<sub>2</sub> conductors at 30 K.

## 4.7 Continuous current characteristics of multifilamentary MgB<sub>2</sub> conductors (In helium vapour)

In the present work transport current measurements of the MgB<sub>2</sub> conductors were done using a closed cycle cryocooler based cryostat or in a liquid helium cryostat. In the cryocooler based measurements the sample was in a vacuum chamber and was cooled by conduction. In the liquid helium dewar or cryostat, the sample was in liquid or vapor helium and was cooled by the direct contact with liquid or vapor helium. In the cryocooler measurements transport currents were passed for short durations only, while in

the liquid helium cryostat measurements the transport currents were passed continuously, with different ramp rates. This section describes the results and analysis of continuous transport current measurements done in liquid helium cryostat. All the measurements were done at the superconductor and magnet division, Institute of Plasma Research (IPR), Gandhinagar.

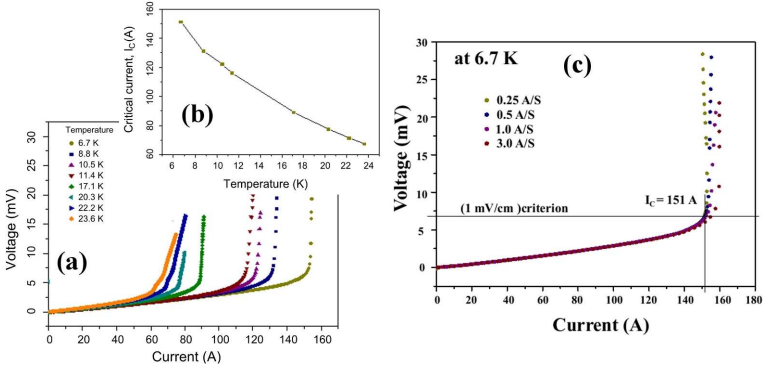


Figure 4.22: (a) I-V plot of a multifilamentary wire at different temperatures, (b) the variation of critical current with temperature and (c) I-V plot for different current ramp rates.

Figure 4.22 (a) shows the I-V plots of a multifilamentary wire at different temperatures. Figure 4.22 (b) shows the plot of critical current ( $I_C$ ) versus temperature for the sample. The measurements were done with current ramp rate of  $\sim 1$  A/S. The sample measured had an outer diameter of  $\sim 2.0$  mm, length of 10.5 cm. The voltage taps were soldered in the middle of the sample with a gap of 6.5 cm between them. The sample shows relatively sharp transition at lower temperatures, but the transition is less sharp or slightly broadened at higher temperatures. In the I-V plot at 6.7 K, the voltage across the voltage tap increases sharply above 151 A. And thus 151 A is taken as the  $I_C$  of the sample at 6.7 K. The sample has  $I_C$  of 151 A 6.7 K, while at 23.6 K the value of  $I_C$  is decreased to 68 A. The value of  $I_C$  of the sample decreases almost linearly with the temperature.

In all the I-V plots, before the sharp rise in the voltage (for currents below  $I_C$ ) a current depended linear background voltage is observed. This background voltage observed is due to the current transfer problem [pages 307-317 of ref: 175]. In principle, for currents far below the critical current

the voltage should be close to zero. This background voltage observed in the samples is due to the current sharing problem between the superconducting filaments and the metallic materials (sheath, matrix and stabilizer), and the problem of current transfer needs special attention for the development of MgB<sub>2</sub> conductor.

In a sheathed conductor, the transport current has to pass through the contact materials (current lead and solder) and also through the metallic sheath before entering into the superconducting core. The penetration of current from the outer core to the superconducting core happens over a length, depending on the nature of the sheath material and the interface between the sheath and superconductor [176, 177, and pages 306, 307 of ref:14]. such a current transfer is accompanied by additional voltage close to the current contact [178, 179].<sup>3</sup>

Figure 4.22 (c) shows the I-V characteristics of the wire measured with different current ramp rates at 6.7 K. The background voltage observed is independent of the current ramp rate at all the temperatures. But the onset of sharp rise in voltage ( $I_C$ ) shows some dependence with the current ramp rate. In general the value of  $I_C$  is slightly higher for measurements done with higher current ramp rate. This behavior is observed for measurements done at other temperatures also.

Two more multifilamentary samples (one wire and one tape) were measured for analyzing the transition details. The details of samples are given in table 4.4. The samples used had four MgB<sub>2</sub> filaments and voltages from

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<sup>3</sup>In a straightforward model of a joint between a metal lead and a superconductor the current in the lead decays exponentially [179, 180] and the current transfer length is approximated as the ratio between the transverse matrix to filament resistance and the longitudinal matrix resistance. So that

$$\lambda = \sqrt{\frac{R_b \times t_n}{\rho_n}}$$

where  $R_b$  is the resistance per unit area of the matrix-superconductor interface and  $t_n$  is the interface thickness and  $\rho_n$  is the longitudinal resistivity of the matrix (sheath). From this equation it is clear that the current transfer length increases with interface resistance and its thickness, which are much higher in the case of multifilamentary conductors. For a typical Fe sheathed mono filamentary MgB<sub>2</sub> conductor the current transfer length will be several (1-4) milli meters [178, 179]. For a multifilamentary conductor (as studied here) there are materials with different resistivities and different interfaces, making the current transfer from the outer sheath to the superconductor much more complex.

two sets of taps from each sample were monitored for studying the nature of transition.

Table 4.4: Details of samples measured for I-V characteristics.

Sample name	Geometry	Cross sectional dimensions	Length (cm)	Distance (cm) between voltage taps	
				Tap 1	Tap 2
MW	wire	$\phi = 2.1$ mm	10.5	6.0	10.0
MT	tape	$3.0 \times 1.2$ mm <sup>2</sup>	7.5	3.7	7.0

Figure 4.23 shows the I-V characteristics of the MW and MT samples, at 15 and 21 K, respectively. Figure 4.23 (a) shows the I-V plots in linear scale and, while figure 4.23 (b) shows the same with the y axis (Voltage) in log scale. For both the samples current is charged at  $\sim 1$  A/s. The sample MW shows a sharp transition at 208.4 A (at 15 K). The transition point is same (208.4 A) for both the voltage taps having gap 6 and 10 cm, and the voltage rises sharply for both the taps above the transition. The similar response in both the voltage taps indicates good superconducting homogeneity along the length of the sample. For the tape sample the transition is less sharp compared to the wire. The transition (voltage rise) started at around 110 A in both the voltage taps and the slop of the curve changed significantly around 150 A.

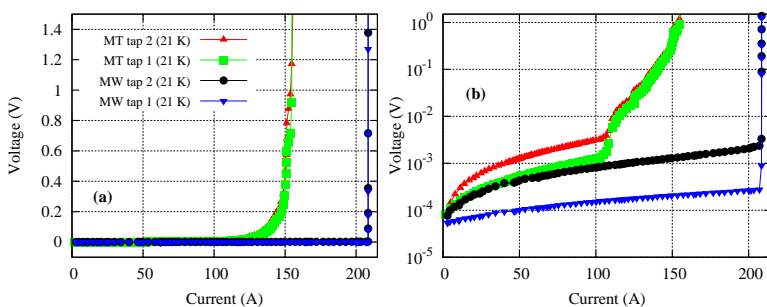


Figure 4.23: I-V plot of samples MW and MT in (a) linear-linear and (b) log-linear scales.

The log scale plot given in figure 4.23 (b) clearly shows the current depended voltage below the sharp rise in voltage. The values of background

voltage were more in tap 2 for both the wire and tape samples. This is expected as the tap 2 has large gap between them and are close to the current contacts than tap 1. So that the current transfer interfered with these readings. The background voltage is more for the tape sample.

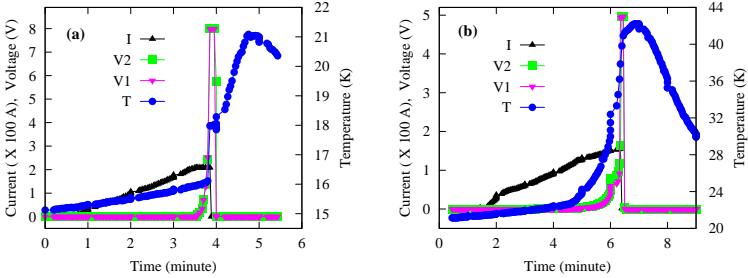


Figure 4.24: Transport current, voltage across taps and the sample temperature during the measurement, for (a) wire and (b) tape sample. Legends are I: Current, V1: Voltage at tap 1, V2: Voltage at tap 2 and T: Temperature.

Figures 4.24 (a) and (b) show the transport current, voltage across the two voltage taps on the sample and the sample temperature during the measurement for the wire and tape samples respectively. The current values are shown in multiples of hundred for clear visibility. For both the wire and tape the two figures show identical behavior (except the values of the parameters). Considering the plot of wire sample, the sample showed an  $I_C$  of 208.4 A as shown in I-V plots. At this value of current the voltage across of both the taps raised sharply. The current sources voltage (not shown here) also rose suddenly for this current and as the power supply voltage reached a preset value (8 V in this case) the current is cut off automatically. Consequently the voltages across the two taps decreased.

The temperature of sample was 15 K at the start of current charging and the temperature linearly increased with current upto  $\sim 208$  A. At this current the sample temperature was 16 K, 1 K above the starting temperature. This increase in temperature is due to the current sharing with resistive matrix and insufficient thermal stability of the composite conductor. The current passing through the normal resistive layers near the current contacts (within the CTL) generates heat. This heat generation at the ends of the composite can cause undesirable quenching of the superconductor at



transport currents much lower than the current it can actually carry. In the present case, at the onset of transition (around 208 A) the sample temperature is 16 K and then there is sudden increase of temperature by  $\sim 2$  K. The sample showed increased temperature even after the current is turned off and the temperature settled at 4 K above the temperature before transition. This shows the sudden quenching and rapid warming of the sample at around the current of 208.4 A.

For the tape sample the rise of temperature was even higher. During the quenching the temperature of the increased from 21 K to 42 K!. This is above the transition temperature of MgB<sub>2</sub>. One thing here to suspect is whether the observed  $I_C$  is a true critical current of the sample or a reduced one due to the temperature increase (insufficient cryostability). These results clearly shows the insufficient thermal stability of the prepared multifilamentary MgB<sub>2</sub> conductors. For the practical use of multifilamentary MgB<sub>2</sub> conductors the thermal stability has to be ensured and there is a great need for further research to address this issue. As observed earlier for the above wire and tape samples the relative area of MgB<sub>2</sub> core is  $\sim 10\%$  and the area of Cu thermal stabilizer is  $\sim 8\%$ . The low thermally and electrically conducting Fe and Ni occupy a significant percentage of the area of the crosssection ( $\sim 82\%$ ). This is the reason for the insufficient thermal stability of the conductors. Future research must be focussed on increasing the Cu and MgB<sub>2</sub> area fraction without sacrificing the strength and quality of the conductor.

## 4.8 Preparation and characterization of MgB<sub>2</sub> conductors by electrical self-heating

In the electrical self-heating method sheathed MgB<sub>2</sub> conductors were prepared by heating the conductor using electric current (either DC or AC), instead of the regular furnace heating. For the electrical self-heating method, mono filamentary wires/tapes were rolled as described in section 4.3. These fabricated wires were then subjected to electrical self-heating by employing a DC current source (Voltage : 0-20 V, Current : 0-30 A).

### 4.8.1 Experimental details

For a typical sample preparation wire sample of length about 50 cm was held horizontally through the axis of a tubular thermal insulator (inside

diameter: 2.5 cm) fabricated from alumina fiber board and the ends of the sample were connected to the current source through a programmable temperature controller, a thermocouple which was kept at the middle of the sample to monitor the temperature. The sample was heated by passing a suitable current through the sample, either manually or automatically through a PC interface. A schematic diagram of the set up used for electrical self-heating is shown in figure 4.25. Figure 4.26 shows the photograph of the set up used to electrically self-heat samples of length 10-30 cm in air. The thermal insulation is removed for clear visibility of the sample.

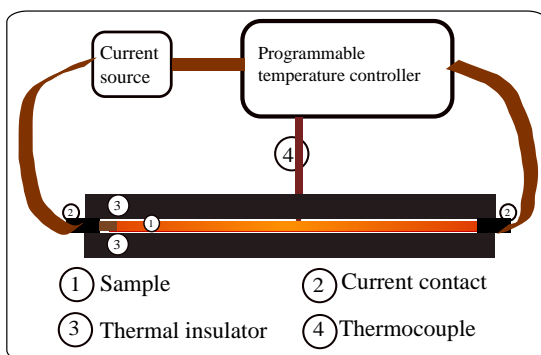


Figure 4.25: Schematic diagram of the preparation of  $\text{MgB}_2$  conductors by electrical self-heating method.

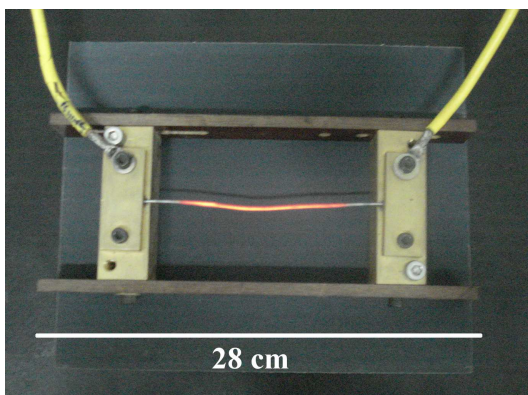


Figure 4.26: Photograph of electrical self-heating of a  $\text{MgB}_2$  conductor.

### 4.8.2 Results and discussion

The results of two monofilamentary wire samples, SW1 with OD = 1.1 mm and length = 40 cm and SW2 with OD = 1.6 mm and length = 25 cm are discussed here. For both the samples the Fe sheath to MgB<sub>2</sub> area fraction is around 80:20. The sample SW1 was heated at 750 °C for 15 minutes and SW2 was heated at 700 °C for 30 minutes. The figure 4.27 shows power schedule for sample preparation for the two typical cases. For SW1 the energy required for one typical experiment is estimated to be about 60 Whr only, of which about 30 Whr (7 V × 17 A × 0.25 hr) is used for soaking for 15 minutes and 30 Whr is used for controlled heating and cooling. The time required for one experiment is typically 45 minutes. For SW2, the total energy required is about 70 Whr, of which ~ 45 Whr is used for soaking at 700 °C for 30 minutes and the remaining 25 Whr is equally shared for heating and cooling. The total time taken for SW2 is one hour. Evidently, the ESH method is highly energy efficient since the electric power is used only for heating the sample alone.

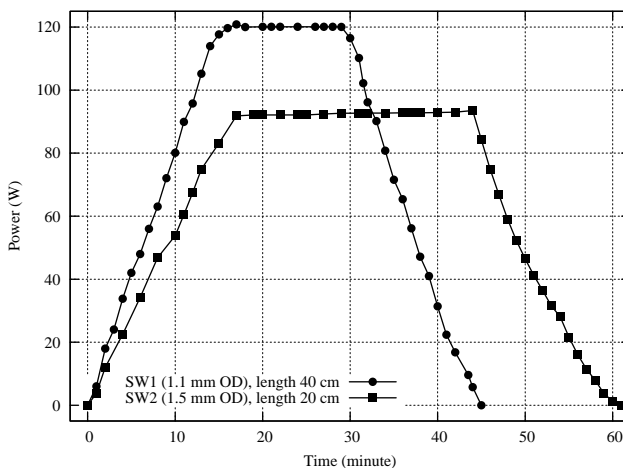


Figure 4.27: Power schedule for typical electrical self-heating experiments.

Figure 4.28 shows the XRD patterns of the wire samples SW1 and SW2 prepared by electrical self-heating method. The XRD patterns reveal that almost phase pure MgB<sub>2</sub> is formed in the samples with very sharp and

strong peaks comparable to that observed in furnace heat treated wire/ tape samples. No peaks of  $\text{Fe}_x\text{B}$  phases are observed here also suggesting that the sintering temperature used here is suitable for the formation of  $\text{MgB}_2$  wires with little or no reaction between Fe and the superconductor matrix. Calculated lattice parameters of the prepared  $\text{MgB}_2$  were obtained as  $a = 3.086 \pm 0.002 \text{ \AA}$  and  $c = 3.524 \pm 0.001 \text{ \AA}$ , which are consistent with values observed for bulks and other furnace heat treated conductors.

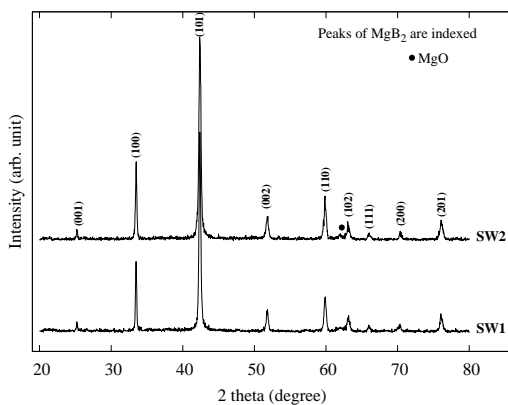


Figure 4.28: XRD spectra of the core of samples prepared by electrical self-heating method.

The  $T_C$  of the samples from R-T measurements were found to be 37.90 K and 38.45 K for SW1 and SW2 respectively. The I-V plots at 25 K for the samples are also shown in figure 4.29. The sample SW1 has a relatively low  $I_C$  due to its smaller cross section. These transport properties are comparable to those of samples prepared with furnace heat treatment. Thus it is demonstrated for the first time that good quality  $\text{MgB}_2$  conductors can be prepared by a simple and energy efficient electrical self-heating method.

The electrical self-heating produces good quality  $\text{MgB}_2$  conductors with crystalline and superconducting properties as good as those of furnace heat treated samples. Most of the electrical self-heating synthesis are done with DC power source. However since AC power source is cheaper the use of AC source is also carried out and the results are found to be identical as that of DC power source.

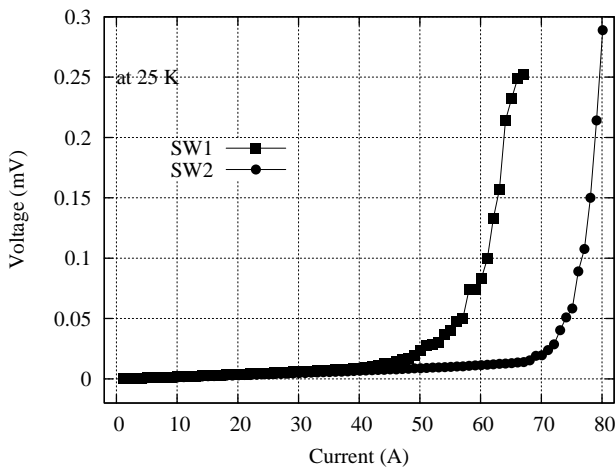


Figure 4.29: I-V plots of samples prepared by electrical self-heating method.

The electrical self-heating method has many advantages such as less power consumption, short preparation time, less preparation cost due to the avoidance of special furnaces with inert gas atmosphere. The method is highly suitable for processes wherein rapid heating or cooling is essential. It is possible to translate the method into a continuous hot rolling process with an array of groove rollers initially for wire making followed by a pair of rollers at the end to which electrical power can be supplied directly. Thus from an industrial point of view the present method is more economical and easy for continuous production of sheathed MgB<sub>2</sub> conductors.

## 4.9 Summary and conclusions

A systematic study on the chemical computability of different sheath materials with Mg/B is conducted and based on the results of the study, Fe is selected as a suitable sheath material for the MgB<sub>2</sub> wire and tape preparation. Fe sheathed MgB<sub>2</sub> wires tapes were prepared by *in situ* Powder-In-Tube method in mono and multifilamentary geometries. The prepared multifilamentary wires were characterized for phase purity and superconducting properties. The prepared multifilamentary conductors have good transport current carrying, comparable to the internationally reported for

MgB<sub>2</sub> conductors. A simple and energy efficient electrical self-heating method is introduced for the preparation of MgB<sub>2</sub> conductors.

## Chapter 5

# Enhancement of in-field critical current density of $\text{MgB}_2$ by selective chemical addition

For technological applications of  $\text{MgB}_2$  superconductor, enhancement of both the in-field critical current density [ $J_C(H)$ ] and upper critical field ( $H_{C2}$ ) are essential.  $\text{MgB}_2$  has high  $J_C$  values in self-field, typically  $10^5$ - $10^6$  A/cm<sup>2</sup> at 4.2 K and  $10^5$ - $10^4$  A/cm<sup>2</sup> at 20-30 K [12, 133], however the  $J_C$  falls sharply in applied magnetic fields, due to weak flux pinning and low upper critical field ( $H_{C2}$ ). In the recent years, significant research is being continued and various techniques have been developed for the improvement of flux pinning and hence  $J_C(H)$  and  $H_{C2}$  of  $\text{MgB}_2$ . Section 1.9 of chapter 1 discusses these issues.

Lattice defects and inclusions of suitable size can act as intense vortex pinning centers [126] and improves the high field performance of  $\text{MgB}_2$  considerably. In  $\text{MgB}_2$ , since lattice structure is rather rigid and the number of elements in the structure is only two, the density of defects introduced by general preparation procedures is too low to provide effective flux pinning. In pristine  $\text{MgB}_2$  flux pinning is mainly provided by grain boundaries. For effective pinning, lattice defects or inclusions can be introduced by a variety of methods like thermo mechanical treatments, irradiation of

high energy particle and chemical doping etc.

Irradiation of high energy radiation introduces atomic scale defects (point or extended) and improves the high field  $J_C$  of MgB<sub>2</sub> considerably [127–129]. Though the  $J_C$  and  $H_{C2}$  increase, the irradiation technique is not easily scalable for large scale production of long length conductors. On the other hand chemical doping is considered to be the most suited and preferred method for the introduction of pinning centers in practical superconductors.

From metallic LTS to cuprate HTS, chemical substitution/addition has been a major approach to improve their superconducting properties. Chemical substitution is easy, favorable for large-scale production compared to other methods used to improve the superconducting properties. Chemical doping, like in other superconductors is an effective and scalable method for modifying the properties of MgB<sub>2</sub>. Based on the nature of the dopant, it can cause substitution at Mg/B site, or react with Mg/B to form reacted secondary phases or can be included in the superconductor matrix without any chemical reaction. All these defects can act as flux pinners and can increase the  $H_{C2}$  and  $H_{irr}$  values and hence enhance the in-field  $J_C$  of MgB<sub>2</sub>.

The final properties of added MgB<sub>2</sub> depend on the chemical nature of the additive, method of introduction and its distribution in the superconductor matrix. Various nano/submicron particles and materials including metallic elements, carbon (in various forms like nanopowders, nanotubes, graphite and diamond), carbides, silicides, nitrides, borides, oxides, and some hydrocarbons have been introduced in MgB<sub>2</sub> (see the recent papers and reviews [84, 85, 130–134] and references therein). These additives improved the flux pinning and  $J_C(H)$  of MgB<sub>2</sub> to different extents. The better results are achieved for C based additives like nano C, diamond, graphite, CNT, SiC, B<sub>4</sub>C and hydrocarbons [84, 85, 130–134]. This is mainly due to the substitution of C at B site<sup>1</sup> which induces lattice disorders and strains, modifies the  $\sigma$  and  $\pi$  band scattering and enhances the  $H_{C2}$  of MgB<sub>2</sub> significantly [69, 181]. Besides the  $H_{C2}$  enhancement, the

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<sup>1</sup>Numerous attempts were made to substitute other elements for Mg and B in MgB<sub>2</sub>. However, MgB<sub>2</sub> has not accepted substitution by other elements except Al, Mn and Sc for Mg site. All these substitutions resulted in a reduction of  $T_C$  of MgB<sub>2</sub> without any considerable improvement on  $J_C$ .



lattice distortions/defects and strains caused by C substitution improves the flux pinning strength also.

The additives selected for the present work include materials commercially available nano particles of rare earth oxides, nano particles of carbides and a non conventional natural material. The materials studied have quite different chemical and physical properties and reactions with Mg/B system. By the selective doping studies a significant enhancement of high field critical current density by nearly two order of magnitude is achieved in technically useful temperatures and fields.

All the samples were prepared by the *in situ* Powder-In-Sealed-Tube (PIST) method as described in chapter 3. The superconducting characterizations (DC magnetization) of the samples were done using a SQUID or VSM based PPMS in collaboration with RRCAT, Indore and JNCASR, Bangalore. Microstructural analyses were done at NIIST using powder XRD, SEM, TEM and EDS measurements.

## 5.1 Influence of nano rare earth oxide (Tb<sub>4</sub>O<sub>7</sub>)

For most of the cuprate based HTS materials addition of rare earth based materials is found to have strong influences on crystalline, microstructural and superconducting properties. Since RE ions are larger than Mg<sup>2+</sup>, they are likely to increase axis length if they are incorporated in the lattice of MgB<sub>2</sub>. From the pressure dependence of axis lengths and  $T_C$  of MgB<sub>2</sub>, this can increase the  $T_C$  [80, 182]. However the substitution of trivalent RE ions for Mg<sup>2+</sup> can decrease the hole density of states (DOS) at the Fermi level of MgB<sub>2</sub> and can decrease the  $T_C$ , as in the case of Al doping (see the extensive review [80] and references therein). Another possible effect of RE doping is a change in critical current density. Although the predominant pinning center in MgB<sub>2</sub> is thought to be grain boundaries, it has been reported that additions of REO introduce REB<sub>4</sub> or REB<sub>6</sub> particles in MgB<sub>2</sub> grains, which would act as pinning centers.

Addition of nano and submicron particles of rare earth oxides (RE oxides) such as Y<sub>2</sub>O<sub>3</sub>, Dy<sub>2</sub>O<sub>3</sub>, Ho<sub>2</sub>O<sub>3</sub> and Pr<sub>6</sub>O<sub>11</sub> are found to increase the flux pinning in *in situ* MgB<sub>2</sub>. Wang *et al* first reported the improvement of  $J_C(H)$  of MgB<sub>2</sub> by nano particles of Y<sub>2</sub>O<sub>3</sub> addition. The addition resulted precipitates of nearly 10 nm size at the grain boundaries and nearly 3-5 nm

sized precipitates uniformly distributed in the MgB<sub>2</sub> grains, which acted as pinning centers. Followed by this, Chen *et al* reported improved flux pinning using submicron sized Dy<sub>2</sub>O<sub>3</sub> as the additive.

Based on these backgrounds, the possibility of RE substitution in MgB<sub>2</sub> is explored, and the influences of REO addition on the lattice parameters,  $T_C$  and  $J_C$  are also investigated. Nano Tb<sub>4</sub>O<sub>7</sub> was chosen as the rare earth oxide and the choice was quite arbitrary.

MgB<sub>2</sub> +  $x$  wt.% of nano Tb<sub>4</sub>O<sub>7</sub> (where  $x = 0, 1, 5$  and  $10$ ) samples were prepared by *in situ* PIST method, using Mg (-325 mesh, 99.8%), amorphous B (-325 mesh, 99%) and nano Tb<sub>4</sub>O<sub>7</sub> (< 60 nm, 99.5%) as starting powders and heat treatment at 800 °C for 2 hours. The samples prepared with 0, 1, 5 and 10 wt.% of Tb<sub>4</sub>O<sub>7</sub> are named as MBTB0, MBTB1, MBTB5 and MBTB10 respectively.

### 5.1.1 Results: Superconducting properties

Figure 5.1 shows the field dependence of magnetic  $J_C$  [ $J_C(H)$ ] of the samples at 5 K, deduced from M-H data. At lower fields the estimation of  $J_C$  is not accurate due to flux jumps. The  $J_C(H)$  is enhanced for all the added samples compared to the undoped sample for the entire field of study. At low fields the improvement in  $J_C(H)$  is higher for samples with lower amounts of Tb<sub>4</sub>O<sub>7</sub> addition, but at higher fields the sample with higher amount of Tb<sub>4</sub>O<sub>7</sub> addition show better  $J_C(H)$  performance. As shown in the table 5.1, at 5 K and 6 T the  $J_C$  of undoped sample is  $1.6 \times 10^3$  A/cm<sup>2</sup>, while it is  $2.6 \times 10^3$  A/cm<sup>2</sup> for the 10 wt.% Tb<sub>4</sub>O<sub>7</sub> added sample. The  $H_{irr}$ , determined by the linear extrapolation to zero for the high field low  $J_C$  segments of the Kramer curves is also improved for the added samples, as shown in table 5.1. At 5 K the  $H_{irr}$  value of undoped sample is 7.5 T, while for the 10 wt.% Tb<sub>4</sub>O<sub>7</sub> added sample it is 8.1 T.

Table 5.1: Superconducting properties of the nano Tb<sub>4</sub>O<sub>7</sub> added samples.

Sample	$T_C$ (K)	$J_C$ at 5 K (A/cm <sup>2</sup> )		$H_{irr}$ at 5 K (T)
		3 T ( $\times 10^4$ )	6 T ( $\times 10^3$ )	
MBTB0	38.6	4.6	1.6	7.5
MBTB1	38.8	6.6	2.4	7.9
MBTB5	38.5	6.9	2.5	7.9
MBTB10	38.6	5.5	2.6	8.1

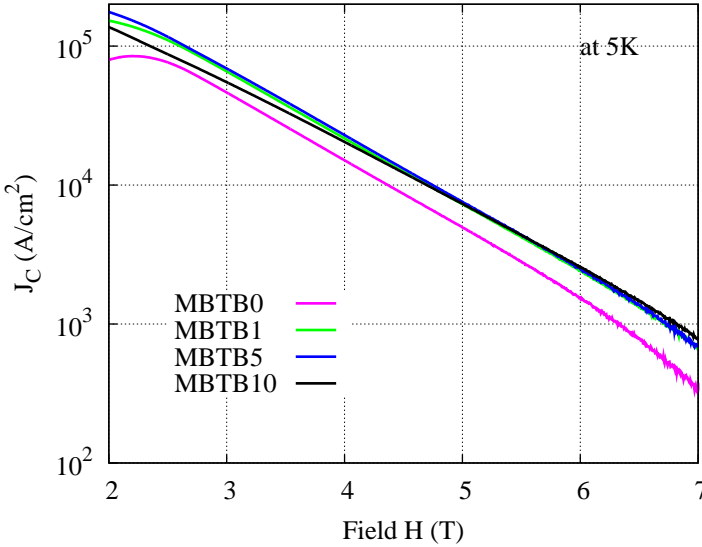


Figure 5.1:  $J_C(H)$  curves of nano Tb<sub>4</sub>O<sub>7</sub> added samples.

The normalized flux pinning force density  $F_P/F_{P_{\max}}$ , where  $F_P = J_C(H) \times \mu_0 H$  as a function of applied magnetic field is plotted in figure 5.2. The flux jumps at low fields have marks on the shape of these curves also. From the figure it is clear that the added samples have enhanced flux pinning compared to the undoped sample. However the sample MBTB1 showed the maximum of  $F_P/F_{P_{\max}}$  at higher fields and the peak position of  $F_P/F_{P_{\max}}$  of MBTB10 is at comparatively lower fields. But at higher fields the  $F_P/F_{P_{\max}}$  of MBTB10 is higher compared to all other samples. This discrepancy in the position of maximum of  $F_P/F_{P_{\max}}$  may be related to the grain connectivity problems and consequent reduced  $J_C$  in low and medium fields in MBTB10 as seen in the  $J_C(H)$  plots. The improvement in  $J_C(H)$  in higher fields and  $H_{\text{irr}}$  of the added samples is due to the enhancement in flux pinning caused by the nano particle addition.

Zero field cooled (ZFC) magnetization plots in the temperature range 5 to 50 K, taken at 20 Oe are shown in figure 5.3. The samples show sharp superconducting transition with  $T_C$  around 38.6 K and  $\Delta T_C < 1$  K. No considerable variation of  $T_C$  is observed for the added samples, indicating

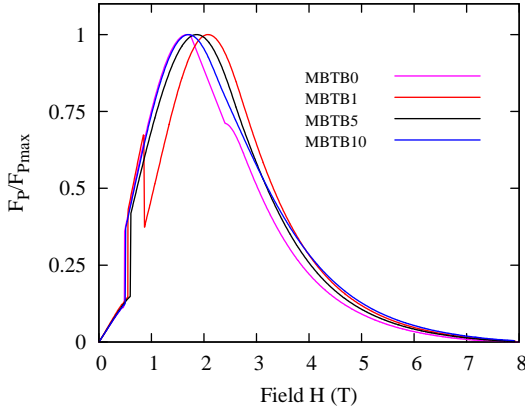


Figure 5.2: Normalized flux pinning force density versus applied magnetic field for nano Tb<sub>4</sub>O<sub>7</sub> added samples.

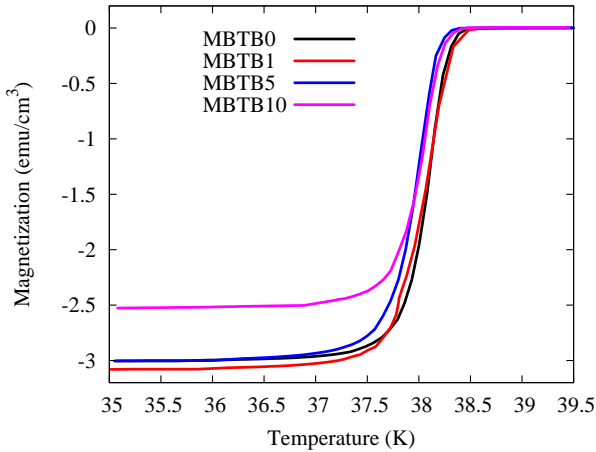


Figure 5.3: ZFC M-T plots of nano Tb<sub>4</sub>O<sub>7</sub> added samples, taken at 20 Oe field.

that the RE is not substituted either at Mg or B site. The consistently  $T_C$  and small  $\Delta T_C$  values show that the samples are of high quality and identical with respect to stoichiometry, lattice strains and the electronic states in the superconducting B planes.

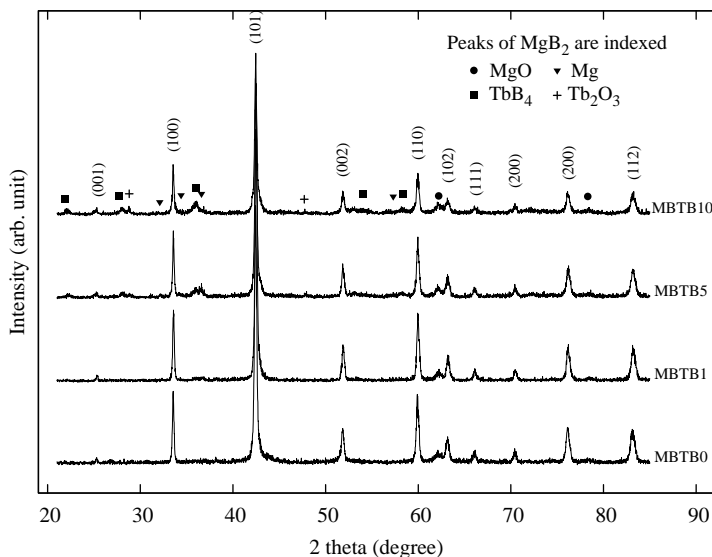


Figure 5.4: Powder XRD patterns of nano  $\text{Tb}_4\text{O}_7$  added samples.

### 5.1.2 Results: Structural properties

Figure 5.4 shows the XRD patterns of  $\text{MgB}_2$  with different amounts of  $\text{Tb}_4\text{O}_7$  additions, heat treated at  $800^\circ\text{C}$  for 2 hours.  $\text{MgB}_2$  is the main phase, with a trace amount of  $\text{MgO}$ , observed in all the samples. No  $\text{Tb}_4\text{O}_7$  is observed even for the 10 wt.% addition.  $\text{TbB}_4$  and  $\text{Tb}_2\text{O}_3$  are found, in increasing amounts with increasing  $\text{Tb}_4\text{O}_7$  additions, in all the added samples. The peak intensities of  $\text{MgB}_2$  are reduced in added samples, indicating that the undoped sample has better phase purity and crystallinity. The presence of  $\text{TbB}_4$  and  $\text{Tb}_2\text{O}_3$  indicates that some of the added  $\text{Tb}_4\text{O}_7$  decomposed and reacted with B at the heat treated temperature. Also for other RE oxide additions in  $\text{MgB}_2$ , their respective borides ( $\text{YB}_4$ ,  $\text{DyB}_4$ ,  $\text{HoB}_4$  and  $\text{PrB}_6$  in  $\text{Y}_2\text{O}_3$ ,  $\text{Dy}_2\text{O}_3$ ,  $\text{Ho}_2\text{O}_3$  and  $\text{Pr}_6\text{O}_{11}$  additions, respectively) are formed and their amounts are found to increase with the increase of added RE oxides [146–149]. The volume percentage of  $\text{MgO}$  in the samples is assessed from the Xray peak intensities and the values are 1.5, 1.8, 2.5 and 3.6 % for MBTB0, MBTB1, MBTB5 and MBTB10 respectively.

Table 5.2: Structural parameters nano Tb<sub>4</sub>O<sub>7</sub> added samples.

Sample	$a$ (Å)	$c$ (Å)	FWHM (degree) of the peaks		Density gcm <sup>-3</sup>
			(002)	(110)	
MBTB0	3.0863	3.5196	0.2843	0.3160	1.32
MBTB1	3.0866	3.5152	0.2986	0.3512	1.41
MBTB5	3.0824	3.5229	0.2784	0.3090	1.47
MBTB10	3.0837	3.5254	0.2647	0.2300	1.46

The  $a$  and  $c$  lattice parameters, calculated from the XRD data, for a hexagonal crystal structure, is given in table 5.2. The maximum standard deviation for  $a$  is 0.002 and for  $c$  is 0.003. The value of  $a$  decreases slightly and  $c$  increases slightly with the addition. 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* [147] for the Y<sub>2</sub>O<sub>3</sub> addition. The FWHM of (002) and (110) peaks of the samples are shown in table 5.2. The maximum variations in the FWHM values are  $\pm 0.008$  degrees. FWHM of both the peaks decreases significantly with doping, except for the samples MBTB1. For MBTB1 the FWHM of both the peaks are significantly larger compared to other samples. The sample showed finer and lower sized grains in the SEM image, which is in agreement with this FWHM values. Lattice strains, resulted from the nano particle addition also have contributions to the significant increase of FWHM of the sample. The geometrical density, also shown in table 5.2, of the samples improved with Tb<sub>4</sub>O<sub>7</sub> addition. Undoped sample showed the minimum density with only 50 % of the theoretical density of MgB<sub>2</sub>.

Figure 5.5 shows the secondary electron SEM images of the fractured surfaces of the samples. All the samples show randomly oriented hexagonal MgB<sub>2</sub> grains of varying size. The homogeneity of microstructure is more for undoped sample, and it decreases with increase of Tb<sub>4</sub>O<sub>7</sub> addition. Undoped sample has grains of average size  $< 1 \mu\text{m}$ . Sample MBTB1 show much finer grains, and this is in agreement with the FWHM results. For samples with higher amounts of additions the grain size increases with increasing Tb<sub>4</sub>O<sub>7</sub>, which is also in agreement with the FWHM results. Some less crystallized (amorphous like) regions are observed in the added samples, which increased with increasing amounts of Tb<sub>4</sub>O<sub>7</sub>.

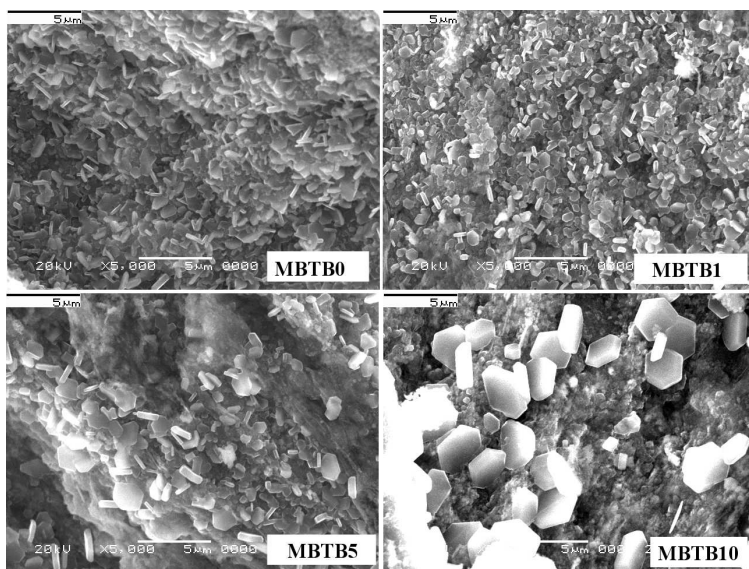


Figure 5.5: SEI SEM of nano  $\text{Tb}_4\text{O}_7$  added samples.

### 5.1.3 Discussion of the results

The  $J_C(H)$  is enhanced for all the added samples, but differently at low and high fields. The  $J_C(H)$  behavior of the samples can be explained in terms of grain connectivity and flux pinning, due to the addition. From figures 5.4 and 5.5 (XRD and SEM) it is clear that the undoped sample has better phase purity, crystallinity and homogeneity in the microstructure. So the observed enhancement in flux pinning and the superconducting properties cannot be attributed to any improvement in any of the above quantities. In  $\text{MgB}_2$ , grain boundaries are strong flux pinners and therefore reduction of grain size improves flux pinning and hence improves the superconducting properties [122, 125]. Finer grains are observed for samples MBTB0 and MBTB1 (undoped and 1 wt.% of  $\text{Tb}_4\text{O}_7$  added sample). However the observed enhancement in  $J_C$  at higher fields is for the samples added with higher amounts of  $\text{Tb}_4\text{O}_7$ . These samples have less homogeneous microstructure and much bigger grain size.

As observed in the XRD patterns the amount of reacted phases such as  $\text{TbB}_4$ ,  $\text{Tb}_2\text{O}_3$  and  $\text{MgO}$  are higher in higher amount of  $\text{Tb}_4\text{O}_7$  added sam-

ples. These phases can be within the MgB<sub>2</sub> matrix and at the grain boundaries. The increased MgO reduces  $J_C$  in low magnetic fields, but improves the  $J_C$  in higher magnetic fields [183, 184]. The increased amounts of reacted phases such as TbB<sub>4</sub>, Tb<sub>2</sub>O<sub>3</sub> and MgO at the grain boundaries reduce grain connectivity and low field  $J_C$ , while these secondary phases act as strong flux pinners at higher fields. This is why the sample MBTB10 showed reduced  $J_C(H)$  in low fields compared to MBTB1 and MBTB5, but improved  $J_C(H)$  in higher fields among the added samples. Thus in the nano Tb<sub>4</sub>O<sub>7</sub> added samples the addition induced secondary phases affects the grain connectivity and flux pinning, and the enhanced flux pinning is the reason for the enhancement in the  $J_C(H)$  and  $H_{irr}$  of the added MgB<sub>2</sub> samples.

### 5.1.4 Conclusion of the addition

Nano Tb<sub>4</sub>O<sub>7</sub> addition is found to be effective in improving the flux pinning properties of MgB<sub>2</sub>, without affecting the  $T_C$  of the system. Better high field  $J_C(H)$  is observed for 10 wt.% of Tb<sub>4</sub>O<sub>7</sub> added MgB<sub>2</sub>. The added nanoparticles and the addition induced normal particles act as strong flux pinners and this is the reason for the improvement in the  $J_C(H)$  of the added samples. Though the nano Tb<sub>4</sub>O<sub>7</sub> addition improved the  $J_C(H)$ , from a practical point of view the improvement is only moderate. So it has become necessary to explore other categories of additives.

## 5.2 Effect of carbon substitution using nano SiC

Since the effect of nano REO on improving  $J_C(H)$  was only moderate, application of other categories of additives became necessary. Considering the significant improvement of  $J_C(H)$  by C based additives nano SiC was chosen as the next additive. The benefit of nano SiC as an additive is first reported by Dou *et al* [142] and is confirmed by many groups worldwide.

MgB<sub>2</sub> +  $x$  wt.% of nano SiC (where  $x = 0, 2, 5, 10$  and  $15$ ) samples were prepared by *in situ* PIST method, using Mg (-325 mesh, 99.8%), amorphous B (-325 mesh, 99%) and nano SiC (< 100 nm, 97.5%) as starting powders and heat treatment at 800 °C for 2 hours. The samples prepared with 0, 2, 5 and 10 wt.% of SiC are named as S 00, S 02, S 05, S 10 and S 15 respectively.



### 5.2.1 Results: Superconducting properties

Figure 5.6 shows temperature dependences of zero-field cooled magnetization for the undoped and SiC added samples in an external field of 100 Oe. Inset of the figure shows plots near the transition region.  $T_C$  is defined as the onset temperature at which the samples exhibit diamagnetic properties and the measured values of  $T_C$  are tabulated in table 5.3. It is observed that the undoped sample has a  $T_C$  of 38.5 K, which decreases systematically with increasing percentage of added SiC and the minimum  $T_C$  obtained for heavily added sample is 35.3 K. The width of superconducting transition,  $\Delta T_C$  of the samples (table 5.3) is found to increase systematically with increasing addition of SiC. This can be attributed to C substitution which reduces crystallinity of the B planes.

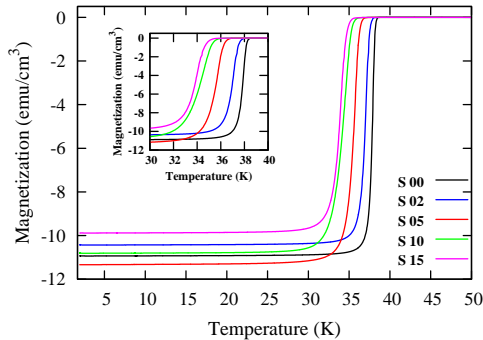


Figure 5.6: ZFC M-T plots of nano SiC added samples, taken at 100 Oe field.

The field dependence for  $J_C$ , calculated from magnetization using the Bean model, at 5 K and 15 K are illustrated in figure 5.7. At 5 K,  $J_C$  jumps abruptly at low fields where the estimation of  $J_C$  may not be accurate due to the flux jump.  $J_C(H)$  behavior of all added samples is significantly enhanced with respect to the pure sample and it is the best for samples S 10 and S 15 at higher fields. Compared to the undoped sample  $J_C$  for 10 wt.% added sample increases by one order at 5 K and  $> 6$  T and at 15 K and 6 T.  $J_C$  values for the same sample (S 10) are  $5.4 \times 10^3$  A/cm<sup>2</sup> at 5 K and 8 T and  $1.8 \times 10^3$  A/cm<sup>2</sup> at 15 K and 6 T. At higher levels of addition the  $J_C(H)$  shows a saturating tendency with almost same behaviour for S 10 and S 15. The  $J_C$  enhancement indicates that addition of SiC increases

the amount of pinning centers with respect to the undoped sample.

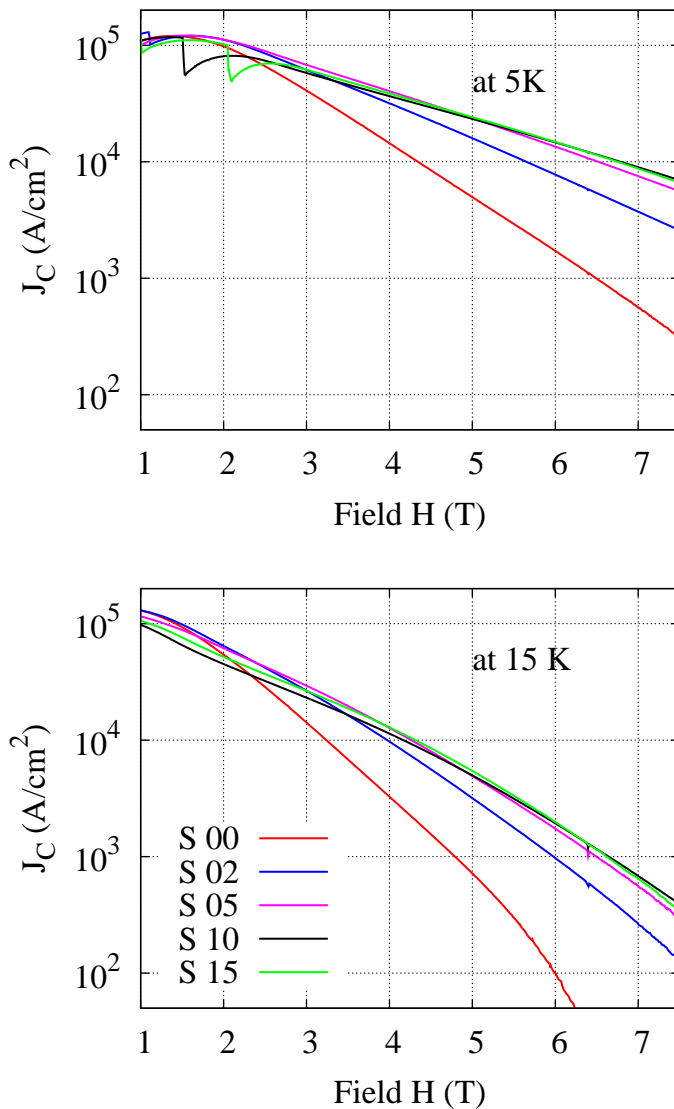


Figure 5.7:  $J_C(H)$  curves of nano SiC added samples.

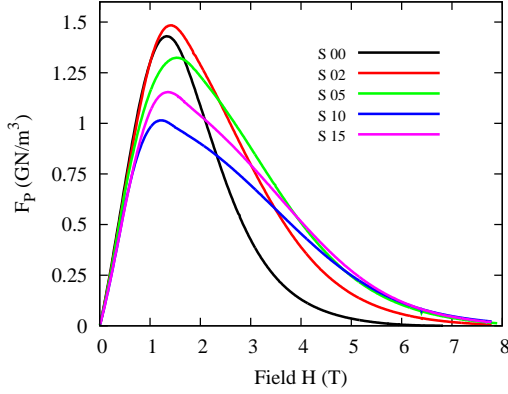


Figure 5.8: Flux pinning force density versus applied magnetic field at 15 K for nano SiC added samples.

The value of  $H_{\text{irr}}$ , determined from the Kramer's curves for the samples is shown in table 5.3. The value of  $H_{\text{irr}}$  is higher for the nano SiC added sample both at 5 K and 15 K. Figure 5.8 plots the field dependence of the volume pinning force,  $F_{\text{p}} = J_{\text{c}} \times H$ , of the samples at 15 K. At higher fields the nano SiC added samples have significantly higher  $F_{\text{p}}$  values compared to the undoped sample.

Table 5.3: Superconducting properties of the nano SiC added samples.

Sample	$T_{\text{C}}$ (K)	$\Delta T_{\text{C}}$ (K)	$J_{\text{C}} (\times 10^3 \text{ A/cm}^2)$ at 5 T		$H_{\text{irr}}$ (T) at	
			5 K	15 K	5 K	15 K
S 00	38.5	1.1	4.9	0.7	8.0	6.0
S 02	38.1	1.4	15.7	3.2	9.6	7.4
S 05	37.2	2.1	23.5	4.9	10.5	8.1
S 10	36.1	2.3	23.6	5.3	11.2	8.5
S 15	35.3	2.5	23.2	5.4	11.1	8.3

## 5.2.2 Results: Structural properties

Powder XRD analysis of pure and SiC added MgB<sub>2</sub> samples shows that the undoped sample consists of single phase of MgB<sub>2</sub> with a trace of MgO as shown in figure 5.9. Peaks of two secondary phases Mg<sub>2</sub>Si and SiC are also

observed in the added samples. Quantitative phase analysis of the samples was also done from XRD data and corresponding volume percentage of  $\text{MgB}_2$ ,  $\text{Mg}_2\text{Si}$ ,  $\text{SiC}$  and  $\text{MgO}$  are tabulated in table 5.4. It is found that increasing the  $\text{SiC}$  doping level resulted increasing the relative amount of non superconducting phases such as  $\text{Mg}_2\text{Si}$  and  $\text{SiC}$  in added samples. This indicates that some of the added  $\text{SiC}$  dissociated into  $\text{Si}$  and  $\text{C}$ , and the  $\text{Si}$  reacted with  $\text{Mg}$  to form  $\text{Mg}_2\text{Si}$  while the  $\text{C}$  is incorporated into the  $\text{MgB}_2$  lattice. No compounds of  $\text{C}$  with  $\text{Mg}$  or  $\text{B}$  are observed in the XRD.

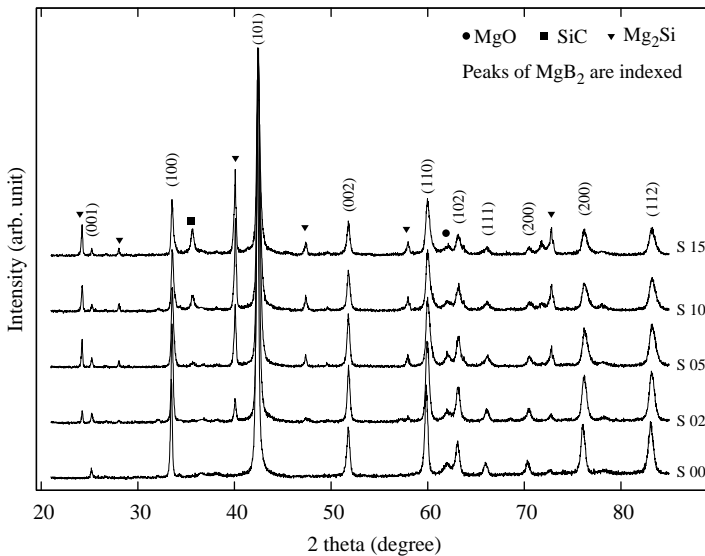


Figure 5.9: Powder XRD patterns of nano  $\text{SiC}$  added samples.

The lattice parameters  $a$  and  $c$  were calculated and the results are shown in figure 5.10. The lattice parameter  $a$  falls sharply for S 02 and S 05 samples and then shows nearly saturating behavior for S 10 and S 15 but no systematic change was observed in the  $c$  lattice parameter. The systematic shrinkage of  $a$  axis with increasing  $\text{SiC}$  doping is caused by carbon substitution for boron. It is to be noted that the presence of unreacted  $\text{SiC}$  is higher for S 10 and S 15 which also implies a nearly saturated behavior of  $\text{C}$  substitution in the  $\text{MgB}_2$  lattice.

Table 5.4: Volume percentages of different phases observed in nano SiC added samples.

Sample	Volume percentage of (%)			
	MgB <sub>2</sub>	MgO	Mg <sub>2</sub> Si	SiC
S 00	98.27	1.73	0	0
S 02	91.00	1.37	6.62	0.98
S 05	78.78	1.35	16.79	3.07
S 10	70.92	1.37	22.28	5.43
S 15	64.88	1.31	26.05	7.75

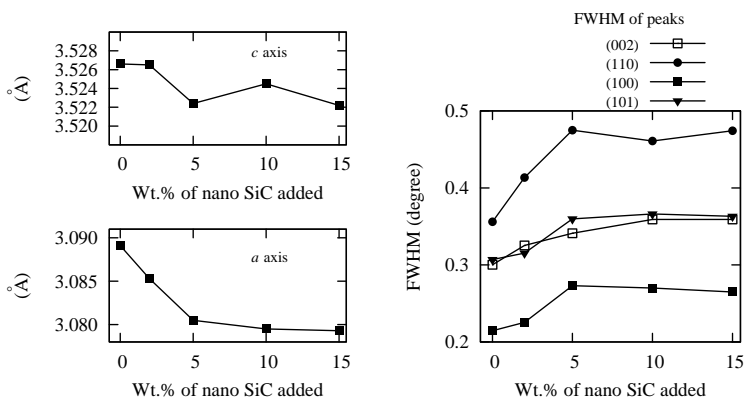


Figure 5.10: Lattice parameters and FWHM of the nano SiC added samples.

Figure 5.10 also shows the variation of full width at half maximum (FWHM) of (100), (101), (002) and (110) peaks of all samples. The data shows a clear and systematic trend with doping. The FWHM of the (001) planes has hardly any effect but the FWHM of (hk0) is the most affected. It can be seen that the values of the FWHM increase gradually up to 5 wt.% of SiC and show a saturating tendency for the heavily added added samples similar to the variation of *a* axis length. Both the observed results on *a* axis variation and the FWHM of (hk0) are in accordance with most of the works reported on the doping studies of SiC or C or other C based additives and is due to the C substitution at B sites.

In the hexagonal structure  $p6/mmm$ , Mg atoms occupy the 1a site (0,0,0) and the B atoms at the 2d site  $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$ . The reported works demonstrate

that C atoms preferentially occupy at the 2d site [69, 185]. This results in the contraction of inplane lattice, since the covalent radii of C is lower than that of B and the availability one extra electron. The lattice strains consequent to the C substitution at B site is responsible for the increased FWHM of the SiC added samples. The reduction of grain size as evidenced from the SEM images can also contribute to the increase of FWHM.

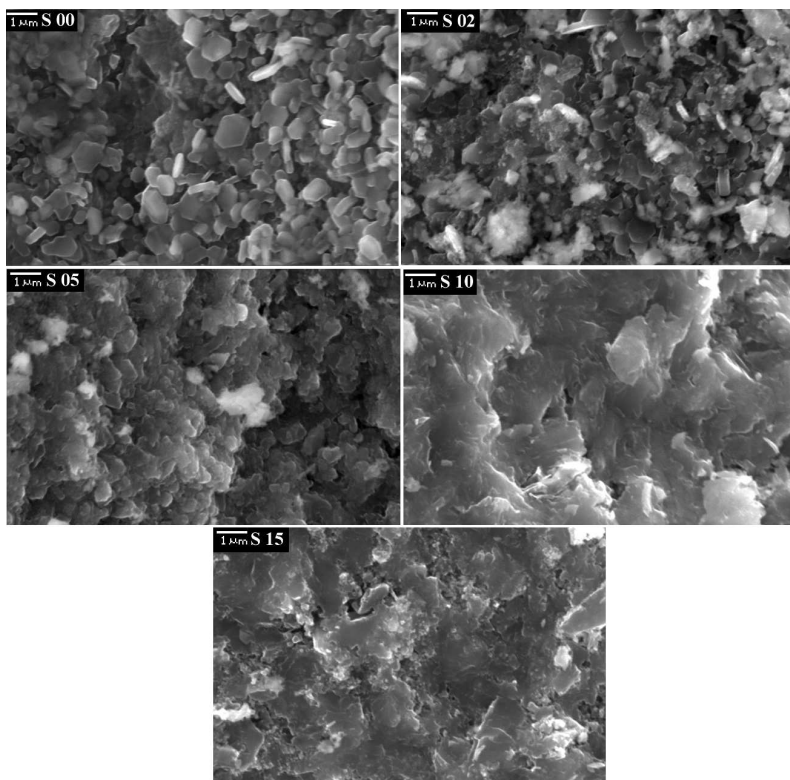


Figure 5.11: SEI SEM of nano SiC added samples.

Figure 5.11 shows the secondary electron SEM images of the fractured surfaces of the undoped and added samples. The undoped sample shows a homogeneous microstructure with tiny and well packed hexagonal grains of average size  $1 \mu\text{m}$  wherein the grain boundaries are sharp and clear. As the level of SiC increases the sharpness of  $\text{MgB}_2$  grain boundaries loses

and the grains become finer. The samples added with 10 and 15 wt.% of SiC show significant difference in microstructure in comparison with pure sample. The samples show a molten like grains without sharp grain boundaries. The presence of large quantity of impurity phases in the system possibly reduces the reaction temperature leading to the formation of molten-like grains in heavily added samples. Although the role of SiC for the formation of these molten-like grains is not fully understood at this stage, its clarification may give some insight into the importance of SiC in  $\text{MgB}_2$ .

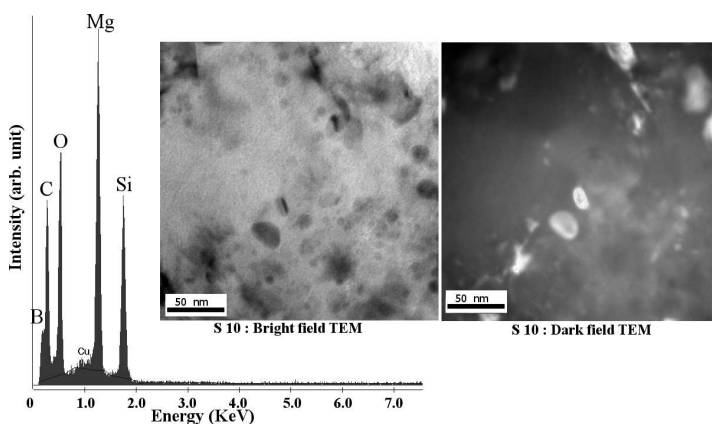


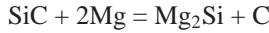
Figure 5.12: Bright and dark field TEM images and EDS spectrum of 10 wt.% of nano SiC added sample.

Typical bright and dark field TEM images of S 10 sample are shown in figure 5.12 and EDS analysis of same sample also given in the image. The images show nano scale inclusions (10-20 nm) within the  $\text{MgB}_2$  grains. These uniformly distributed nano size impurities with size comparable to the coherence length of  $\text{MgB}_2$  can pin the flux lines within the grains. EDS analysis of the selected area confirms the presence of Mg, B, C, Si and O. Analyses of XRD and EDS results suggest that the nano particles within the grains are  $\text{Mg}_2\text{Si}$  and SiC. These provide effective pinning at all the temperature up to  $T_C$ .

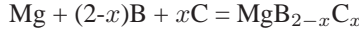
### 5.2.3 Discussion of the results

The addition of nano SiC is found to be very effective in improving the high-field  $J_C$  of MgB<sub>2</sub>. The enhancement of  $J_C$  is so strong that the values of  $J_C$  is enhanced by more than one order of magnitude at higher fields and temperatures. The enhancement of  $J_C(H)$  by nano SiC can be explained by the dual reaction model proposed by Dou *et al* [131].

According to the dual reaction model [131], the nano scale SiC reacts with Mg at a temperature as low as 600 °C to form Mg<sub>2</sub>Si, at the same time releases free atomic scale C as described by the reaction.



The formation of MgB<sub>2</sub> begins to take place at round this temperature and the highly reactive and free C can be easily incorporated into the lattice of MgB<sub>2</sub> via the reaction



As a consequence of the dual reaction taking place at around the formation of MgB<sub>2</sub>, better C substitution takes place as well as the secondary phases such as Mg<sub>2</sub>Si, SiC or C and other Mg-B-Si-C-O precipitates can be effectively embedded within the grains as nano inclusions. The substitution of C at B site at the time of formation of MgB<sub>2</sub> may reduce the grain growth, resulting finer grains and hence increased grain boundary pinning centers.

The substitution of C at B site is evidenced by the reduction of  $T_C$ , decrease of  $a$  axis and in the variation of in-plane FWHM values. The reduction of grain size is observed in the SEM images as well as observed in the increased FWHM values. The nano scale inclusions are clearly observed in the TEM images also. Substitution of C at B modifies the  $\sigma$  and  $\pi$  bands of MgB<sub>2</sub> and hence their scattering rates. The  $H_{C2}$  of MgB<sub>2</sub> is strongly depended on  $\sigma$  and  $\pi$  band scattering rates (both inter and intra scattering), and the value of  $H_{C2}$  in MgB<sub>2</sub> enhances significantly upon tuning of the scattering rates. Thus the improvement of  $H_{C2}$  and better pinning by the nano inclusions are the reasons for the observed significant improvement in the  $J_C(H)$  performance of nano SiC added samples. At higher levels of SiC addition both the C substitution level (as indicated in  $a$  and FWHM



values) and the  $J_C(H)$  shows some saturation tendency, may be indication that C substitution has a major role than the nano inclusions on the  $J_C(H)$ .

### 5.2.4 Conclusion of the addition study

Nano SiC is found to be a suitable additive for improving the high-field  $J_C$  of PIST MgB<sub>2</sub> significantly. Strong enhancement of  $J_C(H)$  of the order of more than one order were observed for SiC added samples at higher fields and temperatures. The addition of SiC caused considerable C substitution at B site, which is responsible for the strong  $J_C(H)$  improvements. Additional pinning centers are provided by the nano scale inclusions of reaction induced secondary phases.

## 5.3 Effect of burned rice husk (BRH): An alternative for nano SiC

Considering the significant improvement in  $J_C(H)$  by nano SiC addition, burned rice husk (BRH) is explored as an alternative low cost replacement for the costly nano SiC. BRH is a nonconventional raw material of SiC which contains ultra fine amorphous silica (SiO<sub>2</sub>) and carbon [186–188]. The ratio of SiO<sub>2</sub> to C in BRH can be controlled by controlling the burning temperature of rice husk. The presence of amorphous SiO<sub>2</sub> in a matrix of friable carbon, easy availability and low cost make BRH a promising dopant for MgB<sub>2</sub>.

The BRH used for addition was prepared by heating the raw rice husk in air at 300 °C for 1 h. Figure 5.13 shows the EDS spectrum of the BRH powder, which shows C (~ 65 at.%), Si (~ 25 at.%) and O (~ 10 at.%) elements in the sample. Inset of the figure shows the powder XRD spectrum of the BRH powder which shows only a broadened peak of SiO<sub>2</sub>, indicating its amorphous nature.

MgB<sub>2</sub> +  $x$  wt.% BRH (where  $x = 0, 5, 10$  and  $15$ ) samples were prepared by *in situ* PIST method, using Mg (-325 mesh, 99.8%), amorphous B (-325 mesh, 99%) and BRH as starting powders and heat treatment at 800 °C for 2 hours. The samples prepared with 0, 5, 10 and 15 wt.% of BRH are named as BRH 00, BRH 05, BRH 10 and BRH 15 respectively.

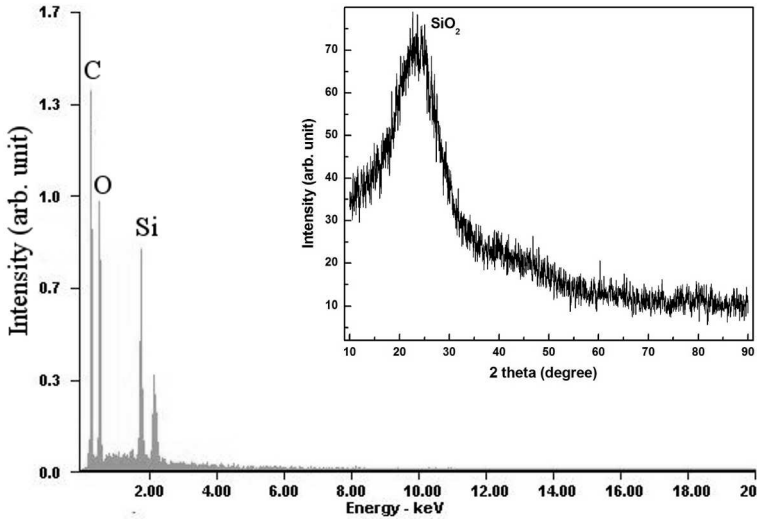
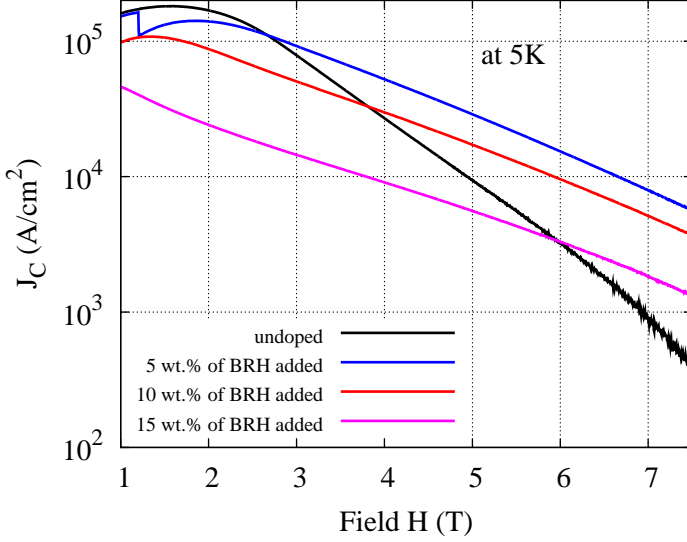


Figure 5.13: EDS spectrum of the BRH powder used for the addition. Inset shows the XRD pattern of the same.

### 5.3.1 Results: Superconducting properties

The field dependence of  $J_C$  calculated from magnetization loops at 5 K is illustrated in figure 5.14.  $J_C$  jumps abruptly at low fields ( $\sim 1$  T) due to the flux jump. The BRH added  $\text{MgB}_2$  samples show enhanced  $J_C$  values at higher applied fields, compared to the pure  $\text{MgB}_2$ . Of all the added samples the 5 wt.% BRH added sample gives the best performance and the level of  $J_C$  enhancement in high magnetic fields is very similar to that of the  $J_C$  increase exhibited by nano SiC addition. For the undoped sample  $J_C$  drops rapidly in the presence of magnetic field but for BRH added samples  $J_C$  values at higher fields increase by more than an order of magnitude. For example the  $J_C$  for 5 wt.% added sample increases by a factor of 40 at 5 K and 8 T as compared to the undoped sample. For the 15 wt.% BRH added sample  $J_C(H)$  is higher only for fields above 6 T, and below 6 T the sample showed low  $J_C$  values compared to the sample BRH 00. This is due to the higher amount of impurities and consequent reduced grain connectivity of the sample, as explained later in the coming sections of this chapter.

ZFC magnetization measurements for the samples in an external field of 20 Oe is shown in figure 5.15 and the measured values of  $T_C$  are tabulated

Figure 5.14:  $J_C(H)$  curves of BRH added samples.

in table 5.5. It is observed that the undoped sample has a  $T_C$  of  $38.51 \text{ K} \pm 0.01 \text{ K}$ , which decreases systematically with increase in dopant level and the minimum  $T_C$  obtained for heavily added (15 wt.%) sample is 35.88 K. This is due to C substitution at boron sites which is consistent with the observed results on variation of  $a$  parameter. The superconducting transition width for a 10% to 90% drop ( $\Delta T_C$ ) is found to be increasing with increasing BRH addition (table 5.5).

Table 5.5: Superconducting properties of BRH added samples.

Sample	$T_C$ (K)	$\Delta T_C$ (K)	$J_C$ at 5 K ( $\text{A}/\text{cm}^2$ )		$H_{\text{irr}}$ at 5 K (T)
			3 T ( $\times 10^4$ )	6 T ( $\times 10^3$ )	
BRH 00	38.51	0.45	7.9	3.2	7.9
BRH 05	37.71	0.52	9.2	15.3	10.3
BRH 10	36.54	1.71	5.1	9.5	10.2
BRH 15	35.88	3.64	1.5	3.3	11.0

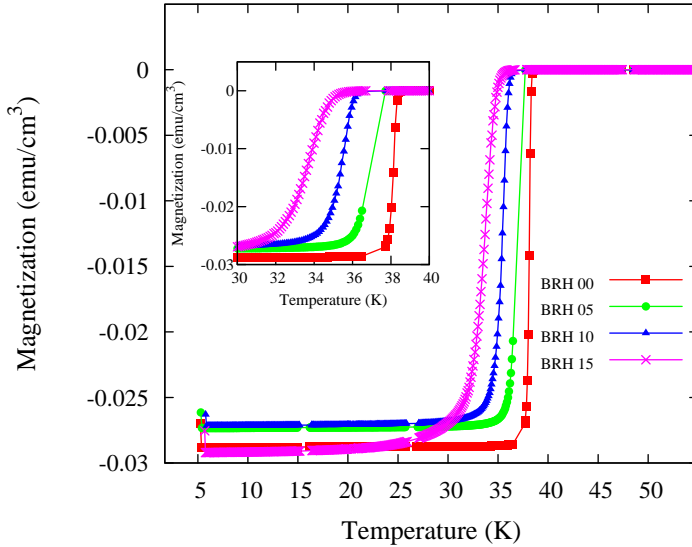


Figure 5.15: M-T plots of BRH added samples.

### 5.3.2 Results: Structural properties

Figure 5.16 shows the XRD patterns of  $\text{MgB}_2$  samples with different levels of BRH addition. The undoped sample consists of mainly  $\text{MgB}_2$  phase with a trace of  $\text{MgO}$  whereas peaks of secondary phases such as  $\text{Mg}_2\text{Si}$ ,  $\text{Mg}_2\text{C}_3$  and  $\text{MgO}$  are observed in the added samples. Quantitative phase analysis of the samples was done from XRD data and corresponding volume percentage of  $\text{MgB}_2$ ,  $\text{Mg}_2\text{Si}$ ,  $\text{Mg}_2\text{C}_3$  and  $\text{MgO}$  are tabulated in table 5.6. On increasing the BRH doping level, the relative amounts of non superconducting phases such as  $\text{Mg}_2\text{Si}$ ,  $\text{Mg}_2\text{C}_3$  and  $\text{MgO}$  are found to be increasing. One aspect here to notice is the significant increase of  $\text{MgO}$  phase as a result of the BRH addition. This is due to the additional oxygen available in the BRH to react with  $\text{Mg}$ . X-ray analysis of BRH shows a broadened peak of amorphous silica (figure 5.13 inset). From the above results, it is clear that in the added samples  $\text{SiO}_2$  and  $\text{C}$  contained in BRH reacted with  $\text{Mg}$  to form  $\text{Mg}_2\text{Si}$  and  $\text{Mg}_2\text{C}_3$  respectively and the remaining oxygen reacted with  $\text{Mg}$  to form  $\text{MgO}$ .

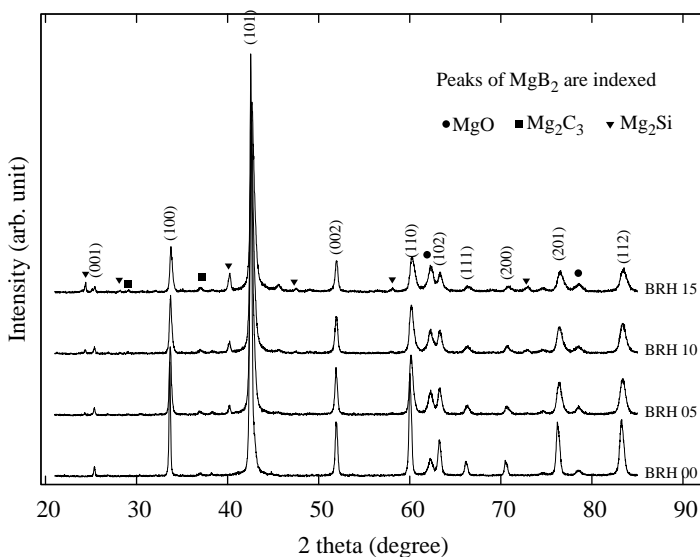


Figure 5.16: Powder XRD patterns of BRH added samples.

Table 5.6: Volume percentages of different phases observed in BRH added samples.

Sample	Volume percentage of (%)			
	$\text{MgB}_2$	MgO	$\text{Mg}_2\text{Si}$	$\text{Mg}_2\text{C}_3$
BRH 00	96.0	4.0	0	0
BRH 05	92.5	5.5	2.4	0.6
BRH 10	88.5	6.0	4.7	3.8
BRH 15	80.2	7.8	9.6	2.4

The lattice parameters  $a$  and  $c$  of the hexagonal  $\text{MgB}_2$  have been calculated and their variations with respect to BRH doping level are shown in figure 5.17. There is a systematic decrease of  $a$  axis with increase in the dopant level. Value of  $c$  axis remains almost unchanged by the BRH addition. The systematic shrinkage of  $a$  with increasing BRH doping is caused by carbon substitution for boron and is explained in the preceding sections.

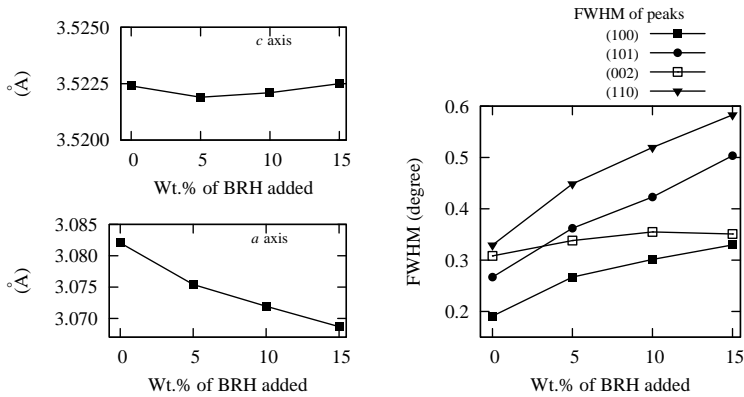


Figure 5.17: Lattice parameters and FWHM of BRH added samples.

Figure 5.17 also shows the full width at half maximum (FWHM) of (100), (101), (002) and (110) peaks of the samples. It is seen that the values of the FWHM sharply vary from pure to added samples except for (002) peak. Because (100) and (110) planes reflect the nature of in-plane honeycomb boron lattice, the broadening of these peaks suggests the occurrence of some distortion in the lattice due to C substitution at B sites. This result is consistent with the earlier reports in which the FWHM of these peaks has a positive correlation with the irreversible field ( $H_{irr}$ ) of  $\text{MgB}_2$ , ie  $H_{irr}$  increases with increasing FWHM [125, 189].

The microstructure of the samples was significantly affected by the BRH addition. Figure 5.18 shows the SEI SEM images of the fractured surfaces of the samples. The sample BRH 00 shows hexagonal faceted grains of average size about  $1 \mu\text{m}$ , typical of  $\text{MgB}_2$  grains. The sample BRH 05 also shows a similar microstructure with faceted grains. The samples BRH 10 and BRH 15 shows some distinct change in microstructure. These samples have a considerable area of impurity like regions and less connected grains. Figure figure 5.19 shows a high resolution TEM image and the corresponding EDS of 5 wt.% BRH added sample. In the TEM image, uniformly distributed nanoinclusions (10-20 nm) are clearly visible within the grain. EDX analysis revealed that the grain contains Mg, B, C, Si and O in accordance with the  $\text{Mg}_2\text{Si}$ ,  $\text{Mg}_2\text{C}_3$  and  $\text{MgO}$  phases observed in the XRD results. the Cu lines observed in the EDS is from the sample grid. These intragrain nanosized inclusions and the crystal defects created by C

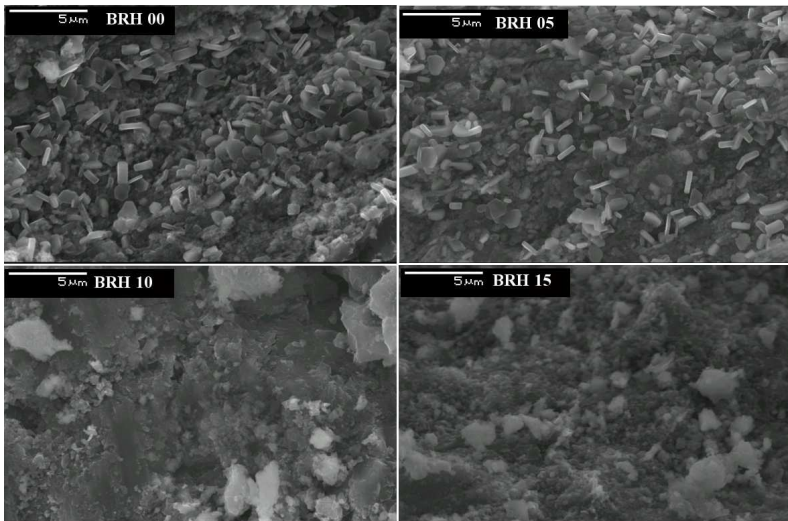


Figure 5.18: SEI SEM of BRH added samples.

substitution serve as strong pinning centers to improve flux pinning.

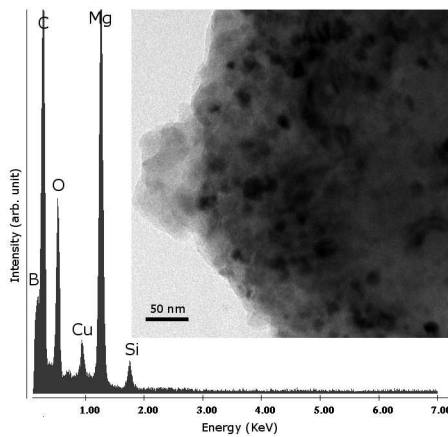


Figure 5.19: EDS and TEM image of BRH 05 (5 wt.% of BRH added) sample.

### 5.3.3 Discussion of the results

The results (Lattice parameters, FWHM and  $T_C$ ) show considerable amount carbon substitution at the boron site, as expected. Significant enhancement of  $J_C(H)$  is observed, especially at higher applied fields, for the BRH added samples. The enhancement due to BRH addition is comparable to that observed for nano SiC added samples. The enhancement of  $J_C(H)$  in the BRH added samples can be understood as a result of the carbon substitution and due to the flux pinning at nano scale intra-grain inclusions). The higher wt.% BRH added samples contain a lot of impurity phases and this is the reason for their low  $J_C(H)$  performance.

### 5.3.4 Conclusion of the addition

Burned rice husk, containing fine amorphous silica and carbon is explored as an additive for effective carbon substitution for enhancing the  $J_C(H)$  of MgB<sub>2</sub>. The BRH addition resulted in significant C substitution as expected and consequently improved the high filed  $J_C$  of MgB<sub>2</sub> significantly. The observed enhancement of  $J_C(H)$  due to the BRH addition is found to be comparable to that of nano SiC addition. Hence BRH is found to be an effective and cheap additive for enhancing the  $J_C(H)$  of MgB<sub>2</sub> superconductor.

## 5.4 Effect of combined addition of nano TiC with nano SiC

According to Dou *et al* [130–132] the additives in MgB<sub>2</sub> can be categorized into four groups. The first group includes additives like nano SiC and carbohydrates which can have both reaction with Mg/B and C substitution. The second group includes materials such as nano C, CNT, and B<sub>4</sub>C which can have C substitution without any reaction. The third group includes materials such as Si, Zr, Ti, RE oxides and silicides which can react with Mg/B without any C substitution, and the fourth group includes materials such as BN, MgO, which do not have any reaction with Mg/B nor any C substitution. From the first group to fourth group the enhancement of  $J_C(H)$  decreases gradually.

Both SiC and TiC are highly thermally stable compounds. When added into the Mg + B system, SiC easily reacts with Mg and releases free C at



a temperature as low as 600-650 °C, which subsequently substitutes for B in MgB<sub>2</sub> [131, 132, 190]. But TiC has no reaction with Mg/B for temperatures  $\leq 850$  °C and the C substitution is comparably small [190]. Even at higher temperatures in Mg + B system it reacts with B to form TiB<sub>2</sub>, rather than with Mg as in the case of SiC. Moreover Ti is found to be a grain refiner in MgB<sub>2</sub> [137, 191, 192]. Thus in MgB<sub>2</sub> both these carbides work differently, have different reactivity with Mg/B and have different extent of C substitution. Hence it is interesting not only to compare the doping effect of SiC and TiC separately but also to find their combined effect in MgB<sub>2</sub>. It is found that the  $J_C(H)$  behaviour is highly enhanced for the codoped samples compared to the undoped as well as the mono added samples. The crystalline and microstructural features of the materials were investigated to correlate with the  $J_C(H)$  performance.

Table 5.7: Sample details : nano SiC and nano TiC addition.

Sample	wt.% of nano particles added	
Name	nano SiC	nano TiC
MBST 00	0	0
MBST 50	5	0
MBST 05	0	5
MBST 2.5	2.5	2.5
MBST 55	5	5

The undoped, monodoped and codoped samples were prepared by *in situ* powder-in-sealed-tube (PIST) method, using Mg (-325 mesh, 99.8%), amorphous B (-325 mesh, 99%), nano TiC (< 80 nm, 98%) and nano SiC (< 100 nm, 97.5%) as starting powders. The samples were heat treated at 850 °C for 2 hours and details of the samples prepared and sample names are listed in table 5.7.

### 5.4.1 Results: Crystalline properties

Figure 5.20 shows the powder XRD patterns of the samples. MgB<sub>2</sub> is the main phase, with a trace amount of MgO, observed in all the samples. Boron rich phases such as MgB<sub>4</sub>, MgB<sub>7</sub> are not observed in any of the samples. Samples added with SiC showed considerable amount of Mg<sub>2</sub>Si and minor quantities of unreacted SiC. For the TiC doping no reacted phase is observed and the TiC as such is observed as unreacted. The formation of

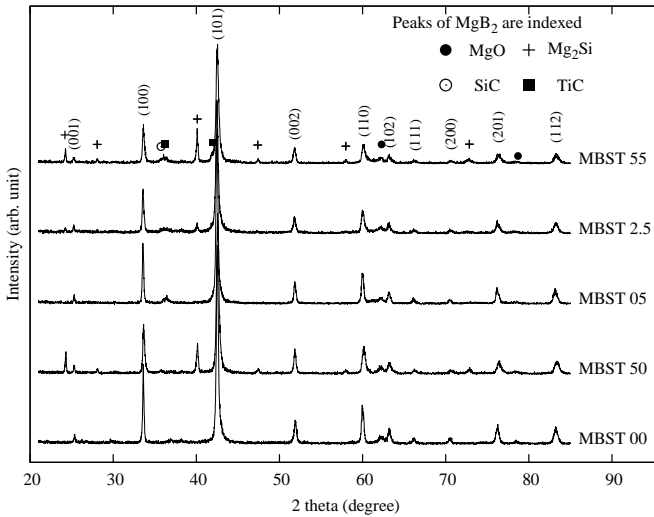


Figure 5.20: Powder XRD patterns of the nano SiC and nano TiC added samples.

$\text{Mg}_2\text{Si}$  in SiC added samples indicates the dissociation of the SiC and the reaction of Si with Mg at the synthesis temperature. In fact this decomposition of SiC and the formation of  $\text{Mg}_2\text{Si}$  phase are reported in almost all the SiC doping studies. SiC starts to react with Mg at a temperature as low as  $600^\circ\text{C}$  [131–133, 190]. Besides the SiC doping, the  $\text{Mg}_2\text{Si}$  is found to form for most of the Si based additives, such as Si, silicides, silicon oil etc on  $\text{MgB}_2$  [193–195]. As stated early, we observed no decomposition of TiC and associated reaction of TiC with Mg/B at our synthesis temperature ( $850^\circ\text{C}/2\text{h}$ ). The detailed study of reactivity of various submicron sized carbides on  $\text{MgB}_2$  bulks by A. Yamamoto *et al* [190, 196] shows that TiC does not react with Mg/B upto  $850^\circ\text{C}$ , but C substitution at B site and formation of small amount of  $\text{TiB}_2$  phase are found at  $950^\circ\text{C}$ .

The volume percentage of different phases formed in the samples is assessed from the integrated Xray peak intensities and is tabulated in table 5.8. The undoped sample has the best phase purity and the highest  $\text{MgB}_2$  volume fraction (98.3 %). The addition of SiC causes more secondary phases, thus reduces the  $\text{MgB}_2$  fraction, than the TiC addition. Minor fractions of MgO are observed in all the samples which are almost same in all cases. The MgO formation may be due to the entrapped air before the end

Table 5.8: Structural properties of the samples: Phase analysis.

Sample	Vol.% of different phases (%)					Relative intensity		Density (g/cm <sup>3</sup> )
	MgB <sub>2</sub>	MgO	Mg <sub>2</sub> Si	SiC	TiC	$\frac{\Sigma(hk0)}{\Sigma(hkl)}$	$\frac{\Sigma(00l)}{\Sigma(hkl)}$	
MBST 00	98.3	1.7	0	0	0	0.306	0.078	1.39
MBST 50	79.0	1.9	18.3	0.8	0	0.251	0.095	1.46
MBST 05	96.6	1.8	0	0	1.6	0.274	0.076	1.41
MBST 2.5	90.2	1.7	6.6	0	1.5	0.254	0.086	1.55
MBST 55	72.1	1.8	21.6	0.9	3.5	0.247	0.095	1.50

sealing of the tubes. The ratio of total intensity of (*hk0*) planes and (*00l*) planes to the total intensity of all the peaks (defined as the relative intensity of (*hk0*) and (*00l*) planes) for the samples is shown in table 5.8. The relative intensity of (*hk0*) planes is slightly reduced and that of (*00l*) planes slightly increased as a result of doping. In the monodoped samples SiC cause more changes in the relative intensity values, than the TiC. The geometrical density, determined by measuring the mass and dimensions of the samples, is also given in table 5.8. The undoped sample has the lowest density of 1.39 g/cm<sup>3</sup>, nearly 50% of the theoretical density of MgB<sub>2</sub>. Among the samples the codoped sample MBST 2.5 show the highest density of 1.55 g/cm<sup>3</sup>.

The crystalline properties of the samples such as lattice parameters, unit cell volume and lattice strains are evaluated using the powder XRD data and are tabulated in table 5.9. The doping - both mono and codoping changed the crystalline features of MgB<sub>2</sub> significantly. The lattice parameters *a* and *c* show systematic variations with the nature and amount of the additives. The changes in lattice parameters with respect to the undoped sample ( $\Delta a$  and  $\Delta c$ ) are more for SiC doping than the TiC doping. The lattice parameter *a* decreases significantly with the SiC doping, while it slightly increases with TiC doping, compared to the undoped one. Among the samples, the mono SiC added sample show the lowest value for *a* axis. For the codoped samples, since SiC has a large impact on *a*, the *a* decreased and its decrease is more in MBST 55 than in MBST 2.5. For the *c* axis both the SiC and TiC caused slight increase compared to the undoped one. Here also as in the case of *a* axis, the variation is more in the SiC doping.

The unit cell volume slightly increases with TiC and slightly decreases with SiC doping. The ratio  $\frac{c}{a}$ , can be used as a measure of lattice distortion, which doesn't show any variation with the TiC doping, but increases with SiC doping.

Table 5.9: Structural properties of the samples: Lattice parameters.

Sample	Lattice parameters and cell volume				Carbon content *
	$a$ (Å)	$c$ (Å)	$(c/a)$	$V$ (Å <sup>3</sup> )	( $x$ in MgB <sub>2-x</sub> C <sub>x</sub> )
MBST 00	3.084	3.518	1.141	28.976	-
MBST 50	3.073	3.524	1.147	28.976	.030
MBST 05	3.086	3.521	1.141	29.039	-
MBST 2.5	3.083	3.524	1.147	28.982	.005
MBST 55	3.080	3.527	1.147	28.976	.010

\* The C content in the added samples is estimated based on the reports of RHT Wilke *et al* [197] and Takenobu *et al* [198], and the averaged data is given.

The Full Width at Half Maximum (FWHM) of selected peaks of the samples are shown in figure 5.21. The data shows a clear and systematic trend with doping. The FWHM of the  $(00l)$  planes has hardly any effect by both the additives, either for mono or codoping. But the FWHM of  $(hk0)$  and  $(hkl)$  planes are affected by the doping:  $(hk0)$  is the most affected plane. As in the case of lattice parameters, here also SiC is mainly responsible for the changes in FWHM values. The FWHM of  $(hk0)$  significantly increases with SiC doping, which is in accordance with most of the works reported on the doping studies of SiC or C or other C based additives and is due to the C substitution at B sites.

In the hexagonal structure  $p6/mmm$ , Mg atoms occupy the 1a site (0,0,0) and the B atoms at the 2d site  $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$ . The reported works demonstrate that C atoms preferentially occupy at the 2d site [69, 185]. This results in the contraction of inplane lattice, since the covalent radii of C is lower than that of B and the availability one extra electron. The lattice strains consequent to the C substitution at B site is also responsible for the increased FWHM of the SiC added samples. In the case of TiC the observed behavior doesn't correlate with the C substitution results. The next possibility is of Ti substitution. But it is known that Ti doesn't occupy the atomic positions (site) in the MgB<sub>2</sub> crystal structure [191, 192]. Even for the Ti added samples Ti either remained as unreacted or reacted with B to form TiB<sub>2</sub> or TiB<sub>4</sub> [191, 192]. So the possibility of Ti going into the lattice structure in our case is remote. Hence, the observed slight variations in the lattice parameters as well as FWHM of TiC added samples may be from the lattice distortions caused by the inclusions of nanoparticles of TiC within the MgB<sub>2</sub> grains, rather than a substitution.

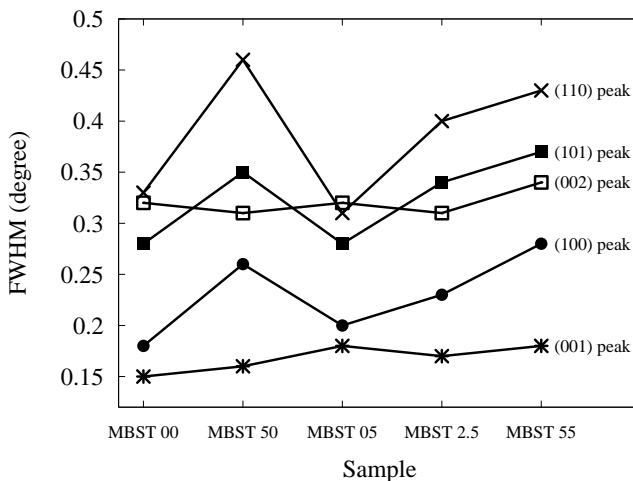


Figure 5.21: FWHM values of selected peaks of the nano SiC and nano TiC added samples.

All the structural features of the samples evaluated above, including phase analysis, relative intensity, lattice parameters and FWHM analysis strongly suggest that the added SiC caused a considerable C substitution at the B site. The SiC caused Mg<sub>2</sub>Si formation also. Meanwhile the TiC remained as unreacted and doesn't cause any substitution in the MgB<sub>2</sub> system. Based on the literature reports of variation of  $a$  axis with C substitution level ( $x$  in MgB<sub>2-x</sub>C<sub>x</sub>) we have estimated the C substitution level in our samples and is listed in table 5.9. The literature data we have used were on polycrystalline samples taken from R. H. T. Wilke *et al* [197] and Takenobu *et al* [198]. The average values of estimated carbon contents are  $x$  around 0.03, 0.005 and 0.01 for the MBST 50, MBST 2.5 and MBST 55 samples respectively.

## 5.4.2 Results: Microstructural properties

The microstructural properties of the samples were investigated using SEM, TEM and EDS analysis. Figure 5.22 shows the SEM images of the fractured surfaces of the samples which show a distinct microstructural change as a result of the doping. The undoped sample shows randomly oriented hexagonal MgB<sub>2</sub> grains with average size of 1-2  $\mu$ m. The undoped sam-

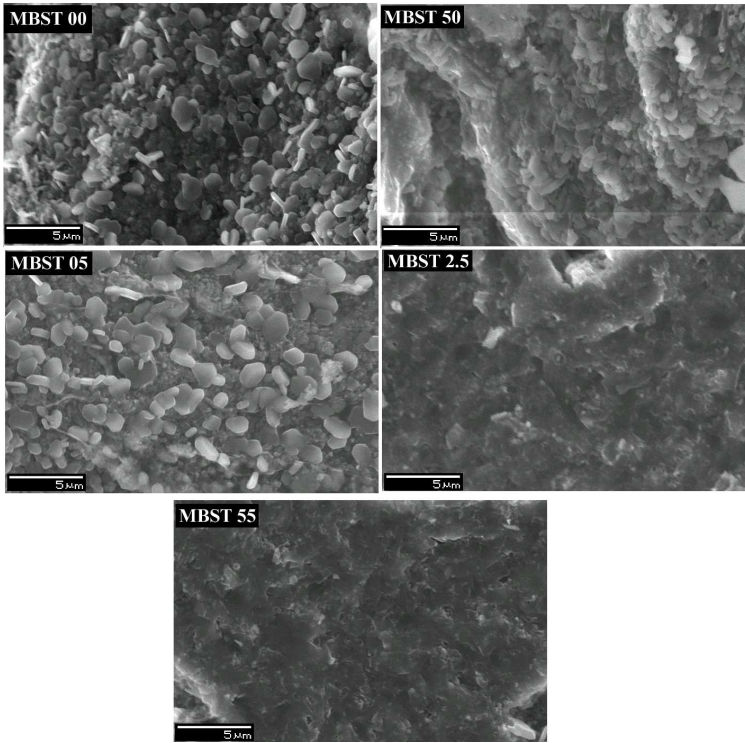


Figure 5.22: SEM images of fractured surfaces of the nano SiC and nano TiC added samples.

ple has grains with considerably sharp grain boundaries, while most of the added samples do not have this feature. The mono SiC added sample (MBST 50) shows a microstructure slightly different from that of undoped sample. The TiC added sample (MBST 05) shows a microstructure similar to that of the undoped sample. The codoped samples show a similar microstructure, distinctly different from that of the above samples. These samples show compacted, more homogeneous microstructure with less defined grain boundaries. This densified microstructure of the codoped sample is in agreement with the higher calculated geometrical density for these samples.

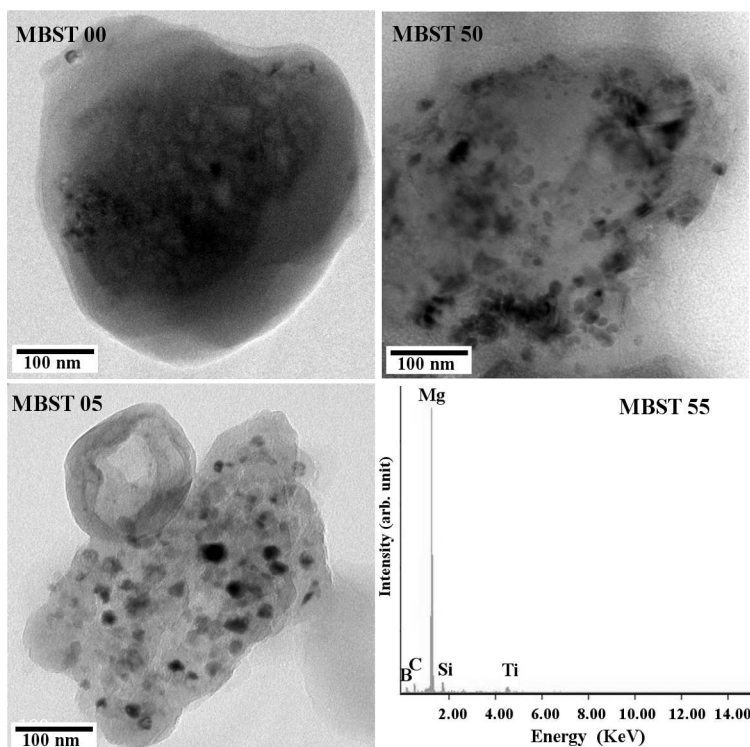


Figure 5.23: TEM images and EDS pattern of selected samples.

Figure 5.23 shows the TEM images of the samples MBST 00, MBST 50 and MBST 05 under identical magnification and the EDS pattern of MBST 55. The images of single grains show microstructural changes due to doping. The image of undoped grain is found to be free of any inclusions. Both the SiC and TiC added samples clearly show nano sized intragrain inclusions. The inclusions of TiC doping are more homogeneous than in SiC doping in which some clustering and agglomeration are observed. In both cases, the average size of the inclusions is around 10 nm. This value is quite comparable with the coherence length of  $\text{MgB}_2$ , and hence these inclusions can act as strong flux pinning centers. The last picture in the figure shows the frame (area) EDS spectrum of the grain in MBST 55 as a typical example. This picture shows the presence of elements Si, Ti, C and O besides Mg and B.

### 5.4.3 Results: Superconducting properties

Figure 5.24 shows the ZFC magnetization curves for the samples, taken at 100 Oe. The inset of the figure shows the region close to the superconducting transition. The undoped sample shows a superconducting transition at 38.44 K.  $T_C$  of the added samples is reduced and the reduction is more for MBST 55. The values of  $T_C$  and  $\Delta T_C$  (defined as the difference of the temperatures corresponding to the 90% and 10% of the maximum shielding signal) are given in table 5.10. For the monodoping SiC reduces the  $T_C$  more than the TiC does. This is expected due to the C substitution at B site. In MgB<sub>2</sub> the B plane is responsible for the superconductivity. The substitution of C at B site reduces the hole concentration and causes changes in phonon modes. The reduced density of states and weakened electron phonon coupling are the reasons for  $T_C$  reduction in the SiC added sample. The TiC mono added sample also shows slightly reduced  $T_C$  (37.85 K). Since no C substitution takes place here the  $T_C$  reduction may be due to the lattice strains caused by the nanometer sized TiC inclusions in the MgB<sub>2</sub>, as lattice strains can also cause slight  $T_C$  reduction in MgB<sub>2</sub> [199]. The  $T_C$  of codoped samples are lower to that of mono added samples and the  $T_C$  is minimum for MBST 55 (37.09 K), the heaviest codoped sample. This is due to the combined effect of both SiC and TiC additives: ie C substitution and lattice strains. The width of transition,  $\Delta T_C$  is minimum for the undoped sample. The value of  $\Delta T_C$  is higher for MBST 50 and comparatively low for MBST 05. In the codoped sample  $\Delta T_C$  is highest for MBST 55. The  $\Delta T_C$  depends on the sample homogeneity, crystallinity etc. The higher  $\Delta T_C$  of MBST 50 is again the result of C substitution, which reduces the inplane (B plane) crystallinity.

Table 5.10: Superconducting properties of the samples - I.

Sample	$T_C$ (K)	$\Delta T_C$ (K)	$J_C$ ( $\times 10^3$ A/cm <sup>2</sup> ) at	
			5 K, 8 T	15 K, 7 T
MBST 00	38.44	1.08	0.17	<0.01
MBST 50	37.43	1.85	3.77	0.52
MBST 05	37.85	1.44	1.32	0.25
MBST 2.5	37.22	1.47	4.90	0.80
MBST 55	37.09	1.73	4.20	0.68

The magnetic field dependence of critical current density of the samples ( $J_C(H)$ ) at 5 K and 15 K are deduced from the isothermal magnetic hysteresis



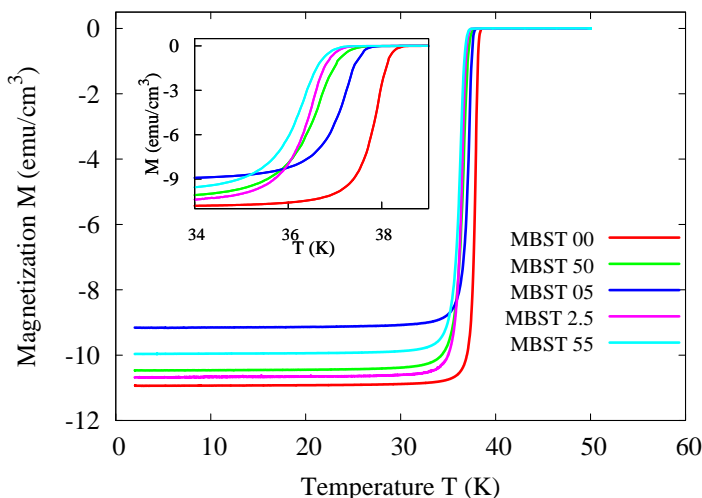


Figure 5.24: ZFC curves of the nano SiC and nano TiC added samples, taken at 100 Oe.

(M-H) measurements. Thermomagnetic flux jumps are observed below 1 T for all samples at 5 K and 15 K. The flux jump is more at 5 K. The variation of  $J_C$  of the samples with field is plotted in figure 5.25. At lower fields the estimation of  $J_C(H)$  may not be accurate due to flux jumps. The  $J_C(H)$  is significantly enhanced for all the added samples both at 5 K and 15 K compared to the undoped sample, for the entire field of study. For the monodoped samples SiC doping shows much improvement in high field  $J_C$ , compared with the TiC doping. However the codoped sample shows the best  $J_C(H)$  performance at higher fields both at 5 K and 15 K. The codoped sample MBST 2.5 shows highly enhanced  $J_C$  values for the entire field of study, both at 5 K and 15 K. The another codoped sample MBST 55 also shows enhanced  $J_C$  values for the entire fields, but at low fields (below 3-4 T) its  $J_C(H)$  is comparable or slightly lower to that of MBST 50. Besides the drastic enhancement of  $J_C(H)$  at high fields for most of the added samples, either monodoped or codoped, the low field  $J_C$  [ $J_C(H), H \rightarrow 0$ ] is better compared to that of undoped sample. This is very important, since for most of the reported works on the enhancement of high field  $J_C$  of MgB<sub>2</sub> exhibit poor low field  $J_C(H)$  performance. The better low field  $J_C$  of the added samples indicates that the grain connectivity is not disturbed

by the doping.

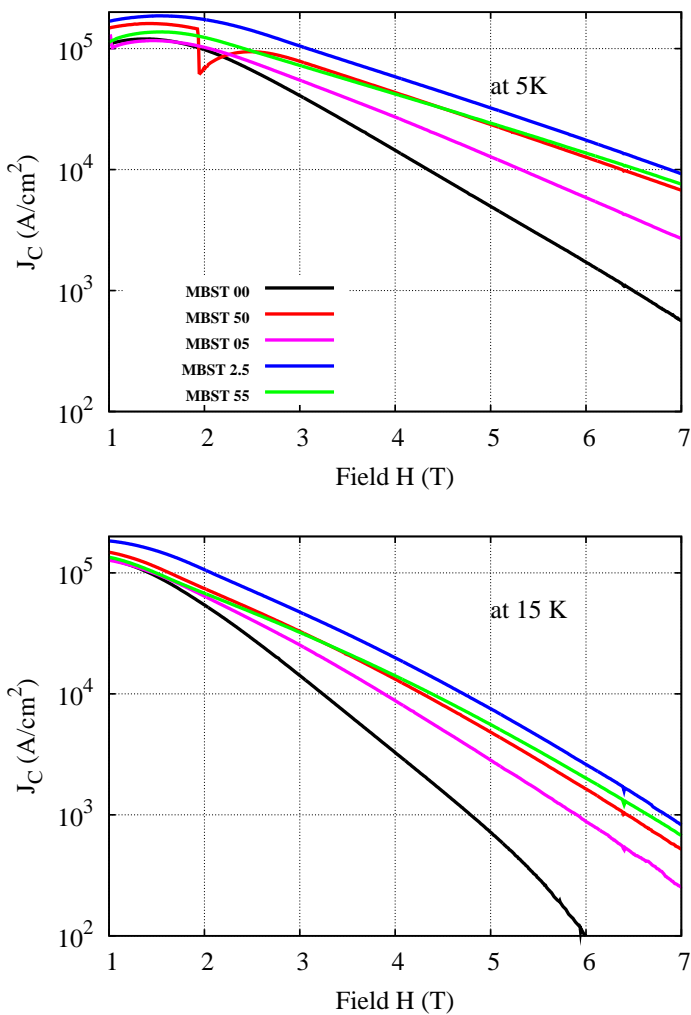


Figure 5.25:  $J_C(H)$  curves of the nano SiC and nano TiC added samples.

The value of critical current density of the samples at selected fields and temperatures is tabulated in the table 5.10. At 5 K and 4 T the  $J_C$  values are  $1.44 \times 10^4$  A/cm<sup>2</sup>,  $4.34 \times 10^4$  A/cm<sup>2</sup>,  $2.72 \times 10^4$  A/cm<sup>2</sup>,  $5.67 \times 10^4$  A/cm<sup>2</sup> and  $4.29 \times 10^4$  A/cm<sup>2</sup> for MBST 00, MBST 50, MBST 05, MBST 2.5 and MBST 55. At 5 K and 8 T the  $J_C$  values are  $0.17 \times 10^3$  A/cm<sup>2</sup> for the undoped sample,  $3.77 \times 10^3$  A/cm<sup>2</sup>, enhanced by a factor of 22 for SiC monodoped sample and  $4.90 \times 10^3$  A/cm<sup>2</sup>, enhanced by a factor of 29 for MBST 2.5, the codoped sample. At 15 K and 7 T the added samples MBST 50, MBST 05, MBST 2.5 and MBST 55 have  $J_C$  values enhanced by a factor of nearly 60, 30, 100 and 76 times, compared to the undoped sample. Thus for the best codoped sample a significant enhancement of  $J_C$  by two orders of magnitude is achieved, at higher temperatures and higher fields (15 K, > 7 T). In general, the sample (MBST 2.5) has  $J_C(H)$  enhanced by 1.5-2.0 times, compared the mono SiC doping (MBST 50) and by 2.0-4.0 times, compared the mono TiC doping (MBST 05). The values of the irreversibility field  $H_{irr}$  of the samples at 5 and 15 K are determined by the linear extrapolation to zero for the high field low  $J_C$  segments of the Kramer curves and is tabulated in table 5.10. The values of  $H_{irr}$  once again reflects the strong enhancement of the superconducting properties as a result of doping. As in the case of  $J_C(H)$  the improvement of  $H_{irr}$  is higher for codoped samples, both at 5 K and 15 K.

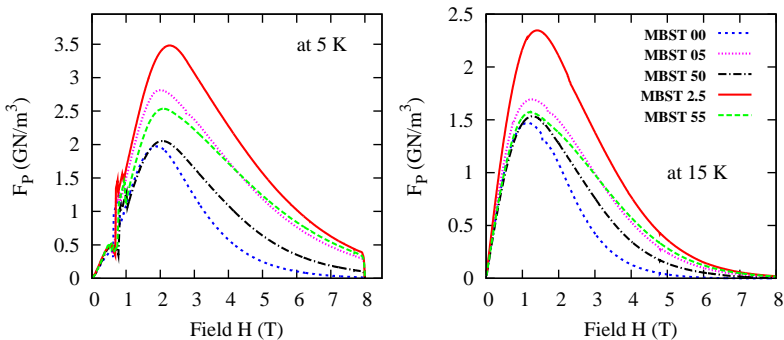


Figure 5.26: Field dependence of flux pinning force density of the nano SiC and nano TiC added samples.

Figure 5.26 shows the bulk flux pinning force density of the samples as a function of the applied field. The flux pinning force density of the

added samples are significantly enhanced and the enhancement is more in the codoped sample. Since the flux jumps shows significant marks on the shape of the curves at 15 K, the curves are plotted after refining the  $J_C(H)$  data between 1 and 2 T. The curves show significantly improved flux pinning force density in the added samples, both at 5 and 15 K. Maximum value of  $F_P$  ( $F_{Pmax}$ ) is 3.48 GN/m<sup>3</sup> and 2.35 GN/m<sup>3</sup> for the best sample (MBST 2.5) at 5 and 15 K, while these values are 1.97 GN/m<sup>3</sup> and 1.47 GN/m<sup>3</sup> for the undoped sample. Also the field at which  $F_{Pmax}$  occurs ( $H_{peak}$ ) is shifted to higher fields in the added samples. The values of  $F_{Pmax}$  and  $H_{peak}$  for the samples are tabulated in table 5.11. These results clearly show the considerable improvement in the flux pinning of the system as a result of doping.

Table 5.11: Superconducting properties of the samples - II.

Sample	$H_{irr}$ (T) at		$F_{Pmax}$ (GN/m <sup>3</sup> ) at		$H_{peak}$ (T) at	
	5 K	15 K	5 K	15 K	5 K	15 K
MBST 00	8.8	6.3	1.97	1.47	1.92	1.14
MBST 50	10.9	8.4	2.81	1.69	2.00	1.26
MBST 05	10.1	7.2	2.05	1.53	2.07	1.25
MBST 2.5	10.9	8.7	3.48	2.35	2.27	1.41
MBST 55	11.1	8.7	2.54	1.57	2.10	1.22

#### 5.4.4 Discussion of the results

The main result of the present work is the significant enhancement in the  $J_C(H)$  performance of MgB<sub>2</sub> superconductor as a result of codoping of nano TiC with nano SiC for the entire range of field studied. Among the additives the nano SiC resulted in considerable C substitution at the B site and formation of reacted secondary phase Mg<sub>2</sub>Si in the matrix. In the case of nano TiC doping the TiC remained unreacted as such and caused no substitutions. Considering the phase purity and crystallinity, the undoped sample is found to be the best. Also it has the highest  $T_C$  among the samples. But it has the lowest flux pinning force and the lowest  $J_C(H)$  performance. Thus the observed enhancement of flux pinning and in-field  $J_C$  of the added samples cannot be due to any improvements in phase purity or crystallinity.

The  $J_C(H)$  of MgB<sub>2</sub> is controlled by both intragranular and intergranular properties. The main intragranular (or intrinsic) factors affecting the

$J_C(H)$  of MgB<sub>2</sub> are upper critical field ( $H_{C2}$ ), flux pinning strength, and to some extent the anisotropy of superconductivity. Grain connectivity, which controls the efficiency of superconducting current to transport from grain to grain is the main intergrain (extrinsic) factor. Among these various factors, the enhancement of  $H_{C2}$  and improvement of flux pinning by homogeneously distributed pinning centers are most important. The  $H_{C2}$  of MgB<sub>2</sub> is strongly depended on  $\sigma$  and  $\pi$  band scattering rates (both inter and intra scattering), and the value of  $H_{C2}$  in MgB<sub>2</sub> enhances significantly upon tuning of the scattering rates [200, 201]. For the improvement of flux pinning homogeneously distributed normal particles of suitable size must be introduced in MgB<sub>2</sub>.

The bulk polycrystalline MgB<sub>2</sub> samples prepared without any externally introduced (pristine sample) pinning centers will be moderately pinned by the grain boundaries. In general, the introduction of additives in MgB<sub>2</sub> can have the following effects.

- (1) increase the  $H_{C2}$  and  $H_{irr}$  by lattice substitutions (which alter the band scattering rates).
- (2) increase the density and strength of flux pinning centers by homogeneous inclusions (either reacted or unreacted impurities).

The enhancement of  $J_C(H)$  in MgB<sub>2</sub> by SiC doping is explained by the dual reaction model [131, 132]. Based on this model the C substitution at B site results strong  $H_{C2}$  enhancement due to band scattering modifications (effect 1 described above) and causes the improvement in  $J_C(H)$ . Further improvement is provided by the flux pinning of unreacted nanoscale SiC and the reacted secondary phase Mg<sub>2</sub>Si, as described in effect 2. There can be unreacted B left as a result of the C substitution and consumption of Mg for the formation of Mg<sub>2</sub>Si. So far no serious attention is given to this issue in SiC added case. If the unreacted B causes some non stoichiometry, it will also cause  $H_{C2}$  enhancement as described elsewhere [94]. Detailed analysis on SiC added MgB<sub>2</sub> samples shows evidences for the formation of secondary phases containing Mg, Si, B, O, C elements. The presence of amorphous BO<sub>x</sub> phases is also considered [202, 203]. These phases are considered to act as additional flux pinning centers. However these phases can limit the superconducting volume fraction and can reduce the grain connectivity if located at the grain boundaries rather residing inside the grains.

In the TiC added samples no substitution is observed. So the effect 1 will be negligible in the sample, and this may be the reason for relatively

small improvement of  $J_C(H)$  in MBST 05 compared with MBST 50. The unreacted residual TiC in nanoscale can act as strong flux pinning centers, as described in effect 2. The TEM image of MBST 05 shows fine homogeneously distributed nanometer sized inclusions, also favors this argument. Thus for the enhancement of  $J_C(H)$  the major contribution in SiC is effect 1 and in TiC is effect 2. On the other hand, for effect 1 SiC is a better dopant and effect 2 TiC is better. Here the nano SiC acted as a group-I dopant, ie as C source and reactive dopant and TiC acted as a group-IV dopant, ie nonreactive and non C source. In the codoped samples both the effects of SiC and TiC may be active, and this is the reason for its better performance compared with the undoped and monodoped samples. Besides the improvement of  $H_{C2}$  and flux pinning, grain connectivity may also be better for the added samples. The codoped samples have denser and compacted microstructure compared with the undoped sample. The low field  $J_C$  of the samples is not deteriorated by doping, and the codoped samples have high  $J_C(H)$  values in spite of large amounts of garbages.

### 5.4.5 Conclusion of the addition study

The effects of two carbides - SiC and TiC in nano particle form, on the structural and superconducting properties of  $\text{MgB}_2$  are studied. The behaviour of these additives in the Mg + B system is compared and the codoping of these two materials in the system is also explored with respect to the crystalline, microstructural and superconducting properties. It is found that both these additives have different reactivity and hence different crystalline and microstructural influences on  $\text{MgB}_2$ . The superconducting properties of added  $\text{MgB}_2$  also differ for the two additives. SiC caused considerable amount of C substitution at B site and formed nano size intragrain inclusions of  $\text{Mg}_2\text{Si}$ . While TiC remains unreacted and does not induce any substitution. Considering the  $J_C(H)$  performance, for monodoping SiC is better than TiC. But codoping of TiC with SiC is found to be much more effective for the enhancement of  $J_C(H)$  of  $\text{MgB}_2$  than the mono doping of any one of these additives. Thus it may be fruitful to explore the effects of codoping of impurities of differing nature to the  $\text{MgB}_2$  system to get far better  $J_C(H)$  performance achieved so far by any one type of additives.

## 5.5 Effect of substituting type (carbon based: BRH) and reacting type (REO: nano Ho<sub>2</sub>O<sub>3</sub>) additives

From the above study, codoping of materials with different chemical and physical nature is found to be very effective for enhancing the high-field  $J_C$  of MgB<sub>2</sub>. Here codoping of burned rice husk (BRH) together with a REO on the  $J_C(H)$  of MgB<sub>2</sub> is studied. The preliminary investigation showed that addition of BRH can cause significant C substitution at B site at around 850 °C. Nano Ho<sub>2</sub>O<sub>3</sub> is chosen as the REO for codoping with BRH, since it causes the formation of HoB<sub>4</sub>, which is magnetic in nature.

The undoped, monodoped and codoped samples were prepared by *in situ* powder-in-sealed-tube (PIST) method, using Mg (-325 mesh, 99.8%), amorphous B (-325 mesh, 99%), nano Ho<sub>2</sub>O<sub>3</sub> (< 60 nm, 99.5%) and burned rice husk as starting powders. All the samples were heat treated in air at 850 °C for 2 hours. The wt % of additives added and sample names are given in table 5.12.

Table 5.12: Sample details : BRH and nano Ho<sub>2</sub>O<sub>3</sub> addition.

Sample Name	wt.% of nano particles added	
	BRH	nano Ho <sub>2</sub> O <sub>3</sub>
S 00	0	0
S 50	5	0
S 05	0	5
S 52	5	2.5
S 55	5	5

### 5.5.1 Results: Superconducting properties

Figure 5.27 shows the field dependence of magnetic  $J_C$  [ $J_C(H)$ ] of the samples at 5 K, deduced from M-H data. The  $J_C(H)$  is enhanced for all the added samples compared to the undoped one. The improvement in  $J_C(H)$  in Ho<sub>2</sub>O<sub>3</sub> alone added sample is only moderate compared to the undoped sample. But the BRH doping shows strong improvement in high field  $J_C$ , compared to the Ho<sub>2</sub>O<sub>3</sub> doping. The level of  $J_C$  enhancement by BRH addition in high magnetic fields is very similar to that exhibited by nano SiC, nano C and/or other carbon based additives. The codoped samples S

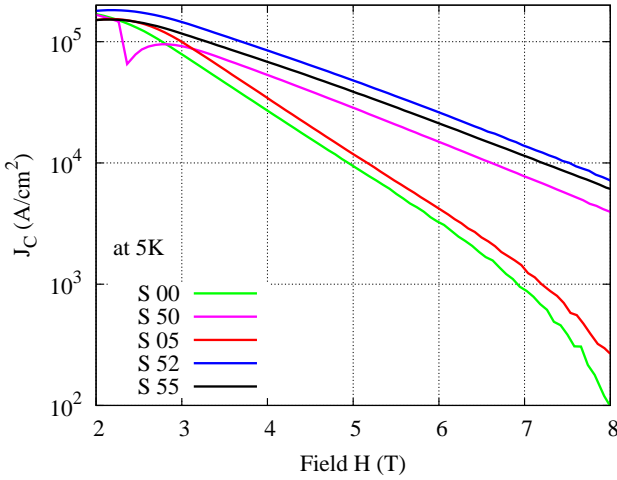


Figure 5.27:  $J_C(H)$  curves of BRH and nano  $\text{Ho}_2\text{O}_3$  added samples.

S 52 and S 55 show still higher  $J_C(H)$  values than the BRH added sample of which S 52 showed the best  $J_C(H)$  performance through out the entire field of study.

As shown in the table 5.13, at 4 T the value of  $J_C$  is  $2.7 \times 10^4 \text{ Acm}^{-2}$ ,  $5.3 \times 10^4 \text{ Acm}^{-2}$ ,  $3.4 \times 10^4 \text{ Acm}^{-2}$ ,  $8.4 \times 10^4 \text{ Acm}^{-2}$  and  $6.8 \times 10^4 \text{ Acm}^{-2}$  for the samples S 00, S 50, S 05, S 52 and S 55 respectively. At 8 T, samples S 50, S 05, S 52 and S 55 have  $J_C$  values enhanced by a factor of 40.8, 2.6, 74.5 and 62.8, compared to the undoped sample. The values of the irreversibility field  $H_{\text{irr}}$  of the samples are determined by the linear extrapolation to zero for the high field low  $J_C$  segments of the Kramer curves and is tabulated in table 5.13. As in the case of  $J_C(H)$  the improvement of  $H_{\text{irr}}$  is highest for codoped samples. Figure 5.28 shows the bulk flux pinning force density of the samples as a function of the applied field. At higher fields, the flux pinning force density of the added samples is significantly enhanced and the enhancement is highest in the codoped sample. At 5 K and 4 T the value of  $F_P$  are 1.1, 2.1, 1.4, 3.4 and 2.7  $\text{GN/m}^3$  for S 00, S 50, S 05, S 52 and S 55, and the values are tabulated in table 5.13.



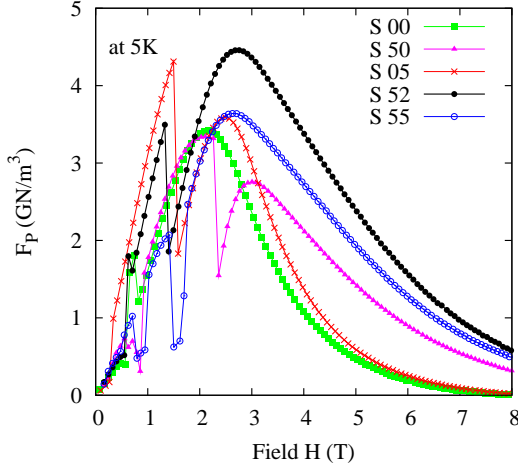


Figure 5.28: Field dependence of flux pinning force density for BRH and nano Ho<sub>2</sub>O<sub>3</sub> added samples.

Table 5.13: Superconducting properties of the samples.  $J_C$ ,  $H_{irr}$  and  $F_P$  values are at 5 K

sample	$T_C$ (K)	$\Delta T_C$ (K)	$J_C$ (A/cm <sup>2</sup> ) at		$H_{irr}$ (T)	$F_P$ at 4 T (GN/m <sup>3</sup> )
			4 T ( $\times 10^4$ )	7 T ( $\times 10^3$ )		
S 00	38.5	0.4	2.7	0.9	8.4	1.1
S 50	38.0	0.9	5.3	7.7	10.2	2.1
S 05	38.4	0.5	3.4	1.3	8.65	1.4
S 52	37.6	1.2	8.4	13.8	11.2	3.4
S 55	37.5	1.1	6.8	11.4	11.1	2.7

ZFC magnetization curves for the samples, taken at 20 Oe are shown in figure 5.29. The undoped sample shows a superconducting transition at 38.5 K, with a  $\Delta T_C$  of 0.4 K. For the Ho<sub>2</sub>O<sub>3</sub> addition the  $T_C$  and  $\Delta T_C$  are almost same as those of the undoped sample, indicating that the Ho ion is not substituted into the Mg/B sites. Generally most of the RE ions (especially Ho) do not substitute at the Mg/B site, due to their large ionic radii compared to Mg and/or B. The  $T_C$  of the BRH added sample (S 50) is reduced by 0.5 K. This reduction is due to the C substitution, however the observed reduction is smaller compared to other C based doping studies

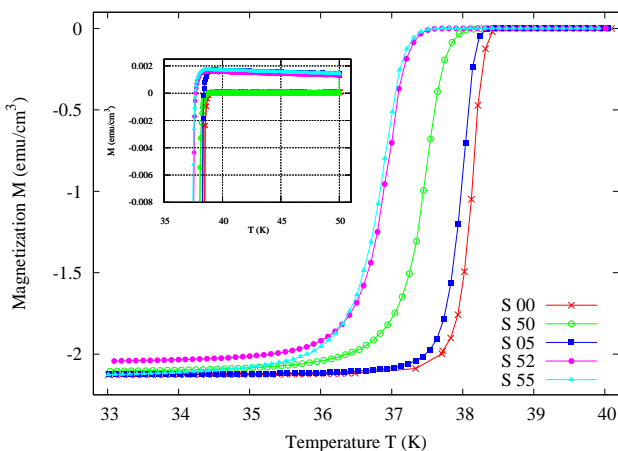


Figure 5.29: ZFC M-T plots of BRH and nano Ho<sub>2</sub>O<sub>3</sub> added samples, taken at 20 Oe field.

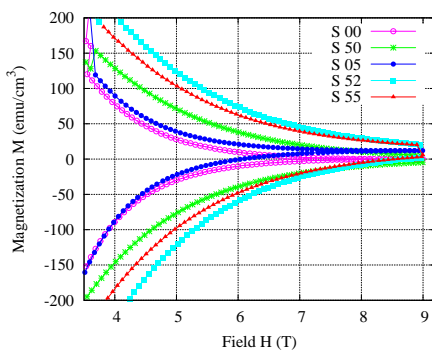


Figure 5.30: Section of M-H plots of BRH and nano Ho<sub>2</sub>O<sub>3</sub> added samples.

[69]. In the codoped samples the value of  $T_C$  is further reduced, may be due to the presence of higher amounts of non-superconducting secondary phases.

The value of  $\Delta T_C$  is higher for BRH addition and comparatively low for Ho<sub>2</sub>O<sub>3</sub> addition. In the codoped samples  $\Delta T_C$  is still higher. The  $\Delta T_C$  depends on the sample homogeneity, crystallinity etc. The higher  $\Delta T_C$  of S

50 is again the result of C substitution, which reduces the inplane (B plane) crystallinity.

Inset of the figure 5.29 shows the ZFC magnetization curves enlarged near the transition region. Samples added with Ho<sub>2</sub>O<sub>3</sub> show a considerable positive magnetic moment ( $M > 0$ ) in the normal state. This is expected as the Ho<sub>2</sub>O<sub>3</sub> samples have the reacted phase HoB<sub>4</sub>, which has a strong magnetic moment. The magnetic behavior of HoB<sub>4</sub> is observed as a superposed paramagnetic background in the magnetization hysteresis loops of S 05, S 52 and S 55 samples (figure 5.30) also.

### 5.5.2 Results: Structural properties

Figure 5.31 shows the powder XRD patterns of the samples. MgB<sub>2</sub> is the main phase, with a trace amount of MgO, observed in all the samples. Significant amount of HoB<sub>4</sub> is observed in samples added with Ho<sub>2</sub>O<sub>3</sub> and slight amounts of Mg<sub>2</sub>C<sub>3</sub> and Mg<sub>2</sub>Si are observed in BRH added samples. No Ho<sub>2</sub>O<sub>3</sub> or other Ho containing phase is observed in the Ho<sub>2</sub>O<sub>3</sub> added samples. As stated earlier BRH contains amorphous silica and C, available for reaction. It seems that Si and C contained in the BRH reacted with Mg to form the Mg<sub>2</sub>Si and Mg<sub>2</sub>C<sub>3</sub> phases. It is reported that Mg<sub>2</sub>Si forms in most of the Si based additives, such as nano-SiC, Si, silicides, silicon oil etc on MgB<sub>2</sub> [193–195] and has a significant role in improving the flux pinning. Formation of Mg<sub>2</sub>C<sub>3</sub> is also reported in carbon based doping studies [140, 204]. No detectable amount of SiO<sub>2</sub> is observed in the BRH added samples. The presence of HoB<sub>4</sub> indicates that some of the added Ho<sub>2</sub>O<sub>3</sub> decomposed and reacted with B at the heat treated temperature as reported earlier in the case of other REO doping [146–149]. In the codoped samples HoB<sub>4</sub>, Mg<sub>2</sub>Si and Mg<sub>2</sub>C<sub>3</sub> are observed as secondary phases, besides MgO. No additional reacted phases are observed as a result of codoping.

The volume percentage of MgB<sub>2</sub> and MgO phases formed in the samples is assessed from the integrated Xray peak intensities and is tabulated in table 5.14. The undoped sample has the best phase purity and the highest MgB<sub>2</sub> volume fraction. Volume percentage of MgO is minimum in the undoped sample and is maximum in highly codoped sample. Minor fractions of MgO observed in the undoped sample is due to the entrapped air before the end sealing of the tubes. The oxygen available in BRH and Ho<sub>2</sub>O<sub>3</sub> is responsible for the increased amount of MgO in the added samples.

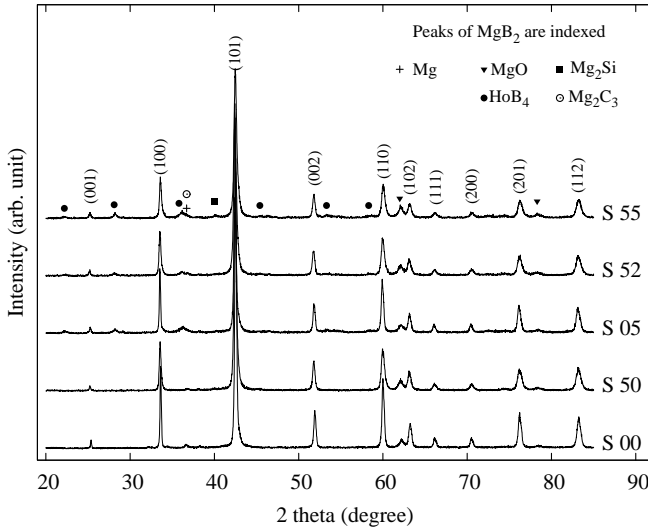
Figure 5.31: XRD patterns of BRH and nano Ho<sub>2</sub>O<sub>3</sub> added samples.

Table 5.14: Crystalline properties of the samples

Sample	Vol. of (%)		Lattice parameters			Carbon <sup>1</sup> content	grain size	strain <sup>2</sup> (%)
	MgB <sub>2</sub>	MgO	<i>a</i> (Å)	<i>c</i> (Å)	<i>c/a</i>			
S 00	97.3	1.6	3.084	3.525	1.143	-	210	0.80
S 50	95.7	3.1	3.077	3.526	1.146	0.021	140	1.1
S 05	93.7	2.3	3.086	3.522	1.141	-	180	0.8
S 52	93.2	3.6	3.080	3.525	1.144	0.013	90	0.9
S 55	88.2	4.4	3.080	3.529	1.146	0.013	60	0.9

<sup>1</sup> *x* in MgB<sub>2-x</sub>C<sub>x</sub>, estimated based on the data of RHT Wilke *et al* [197] and Takenobu *et al* [198].<sup>2</sup> Lattice strain of (*hk*0) plane is determined from the slop of Williamson-Hall plot (Figure 5.33).

The *a* and *c* lattice parameters, calculated from the XRD data, for a hexagonal crystal structure, is given in table 5.14. The value of *a* decreases considerably and *c* increases slightly with the BRH addition. This is in agreement with other works on carbon based doping and is due to the substitution of C at the B site and is explained elsewhere [69, 205]. For the Ho<sub>2</sub>O<sub>3</sub> addition *a* shows slight increase and *c* remains almost the same, compared to the undoped sample. Here also the observed result is in accordance with other REO additions. For the REO doping it is believed that

RE will not occupy the lattice site of either Mg or B and hence the observed 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. In the codoped samples  $a$  decreases and  $c$  increases compared to the undoped one. Here the C substitution at B site (by BRH doping) is the significant factor for the lattice parameter changes. The ratio  $\frac{c}{a}$ , a measure of lattice distortion, increases with BRH doping, but remains almost unchanged with Ho<sub>2</sub>O<sub>3</sub> doping.

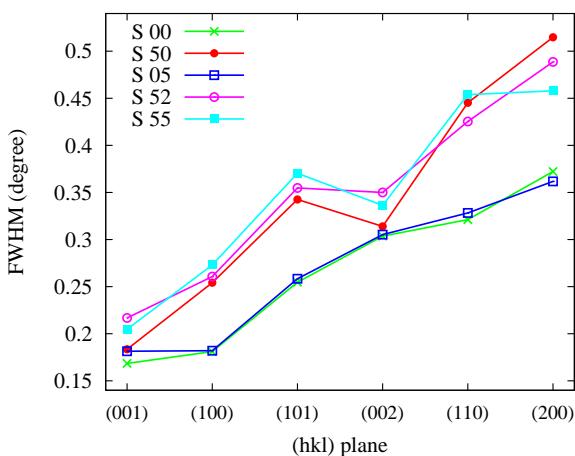


Figure 5.32: FWHM of selected peaks of BRH and nano Ho<sub>2</sub>O<sub>3</sub> added samples.

The Full Width at Half Maximum (FWHM) of selected peaks of the samples are shown in figure 5.32. The data shows a clear and systematic trend with doping. The sample added with Ho<sub>2</sub>O<sub>3</sub> alone shows same FWHM values as that of the undoped sample, while the sample added with BRH shows considerably different FWHM values. The FWHM of Ho<sub>2</sub>O<sub>3</sub> added samples once again confirms that the RE ions are not entered into the lattice sites in MgB<sub>2</sub>. The FWHM of the (00 $l$ ) planes has hardly any effect by the doping, either for mono or codoping. But the FWHM of ( $hk0$ ) and ( $hkl$ ) planes are affected by the doping: ( $hk0$ ) is the most affected. The FWHM of ( $hk0$ ) significantly increases with BRH doping, which is due to the C substitution at B sites.

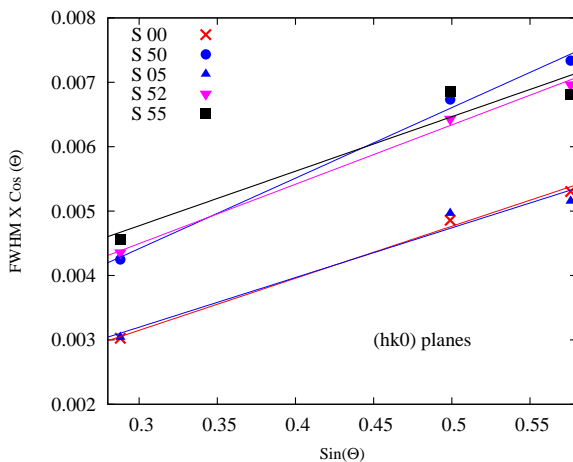


Figure 5.33: Williamson-Hall plots of  $(hk0)$  planes of the samples. Points shows data points and lines are linear fits to the data points.

Figure 5.33 shows the Williamson-Hall plots of the  $(hk0)$  planes of the samples. Using the plots, lattice strain is estimated from the slope and the crystallite size from the y intercept. The estimated lattice strain values for  $(hk0)$  planes for the samples are given in table 5.14. The samples added with BRH have a considerably higher strain value. The sample added with nano  $\text{Ho}_2\text{O}_3$  alone (S 05) has slightly lower strain value compared to that of the pure sample. For the  $(00l)$  planes, both BRH and nano  $\text{Ho}_2\text{O}_3$  addition shows slight reduction in the lattice strain. The particle size (table 5.14) decreases significantly with the addition. The undoped sample has an average particle size of 210 nm, while the samples S 50 and S 05 have particle sizes of 140 nm and 180 nm respectively. For S 52 and S 55 the particle size are still reduced to 90 nm and 60 nm. Thus from the FWHM analysis it is clear that significant in-plane lattice strain occurs by BRH addition. Also both BRH and  $\text{Ho}_2\text{O}_3$  addition causes considerable decrease of MgB<sub>2</sub> grain size.

The SEI SEM images of the fractured surface of the samples (figure 5.34) show distinct and systematic microstructural change as a result of doping. The undoped sample (S 00) shows randomly oriented faceted hexagonal MgB<sub>2</sub> grains with average size of 1-2  $\mu\text{m}$ . Some of the grains in

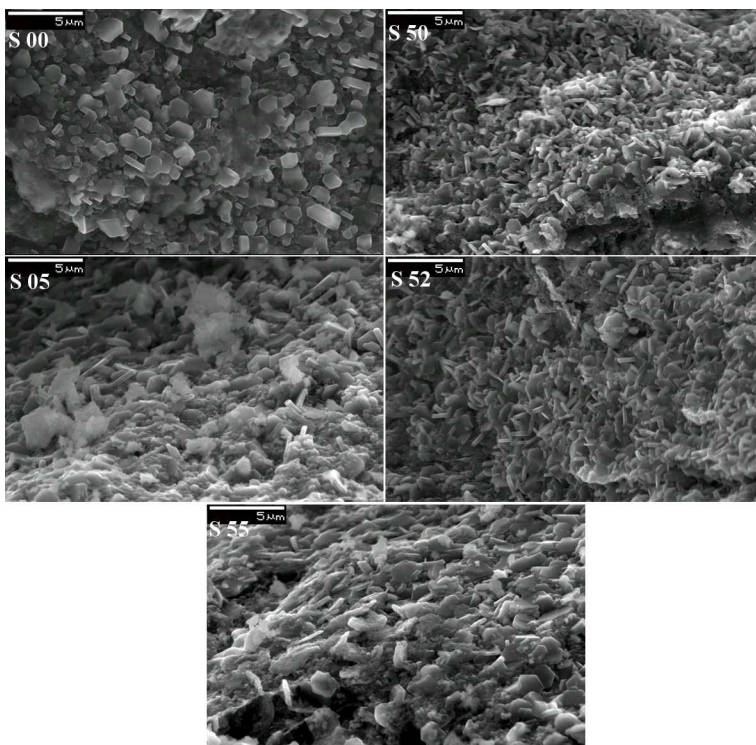


Figure 5.34: SEI SEM of BRH and nano Ho<sub>2</sub>O<sub>3</sub> added samples.

the sample showed sharp grain boundaries, while most of the grains show melt like grain boundaries/connections. The BRH added sample (S 50) has uniformly distributed flaky grains with much smaller size than those in S 00. The small size of the grains of S 50 is in agreement with its observed higher FWHM values. Ho<sub>2</sub>O<sub>3</sub> added sample (S 05) shows a microstructure significantly different from those of the above two samples. Some amorphous like (less crystallized) regions (pockets) are seen in the matrix of this sample. For the codoped samples, the microstructure of S 52 is more like sample S 50, while sample S 55 is more like S 05.

### 5.5.3 Discussion of the results

The  $J_C(H)$  of MgB<sub>2</sub> is improved by the doping of nano Ho<sub>2</sub>O<sub>3</sub> and BRH in mono and codoping conditions. The level of enhancement is more in BRH and less in Ho<sub>2</sub>O<sub>3</sub> addition for monodoped samples. The codoped samples have significantly enhanced  $J_C(H)$  values compared to the undoped and monodoped samples. In the case of bulk MgB<sub>2</sub> superconductor, the in-field critical current density is controlled by parameters like phase purity, crystallinity, grain connectivity, flux pinning etc [84]. From the XRD and SEM results it is very clear that the undoped sample has better phase purity and crystallinity and homogeneity. the undoped sample sample has higher  $T_C$  and low  $\Delta T_C$  values also. So the observed enhancement in flux pinning and the  $J_C(H)$  of the added samples cannot be attributed to a better phase purity, crystallinity and/or homogeneity.

Considering the nano Ho<sub>2</sub>O<sub>3</sub> alone added sample (S 05), the added Ho<sub>2</sub>O<sub>3</sub> reacted with B and formed HoB<sub>4</sub> phase as impurity. The lattice parameters, FWHM as well as  $T_C$  and  $\Delta T_C$  values of the nano Ho<sub>2</sub>O<sub>3</sub> added sample remains almost comparable to that of the undoped sample, indicating that Ho is not entered into the lattice site of either Mg or B. In this sample the pinning is mainly provided by the reacted impurity phase HoB<sub>4</sub>. The strength of pinning force exerted on the flux lines by these pinners may be weak and hence the observed moderate improvement in flux pinning and moderate increase in  $J_C(H)$  in the sample S 05. In other words the main reason for the  $J_C(H)$  improvement in Ho<sub>2</sub>O<sub>3</sub> added sample is pinning alone. For the BRH added sample there is clear evidence of C substitution at the B site and this is the main reason for the strong enhancement in  $J_C(H)$  performance. The reaction induced secondary phases such as Mg<sub>2</sub>Si and Mg<sub>2</sub>C<sub>3</sub> can contribute to further pinning. For the codoped samples both these effects of BRH and Ho<sub>2</sub>O<sub>3</sub> are simultaneously active, i.e., a combination of 'substitution' + 'pinning'. The BRH addition improves  $H_{C2}$  and the magnetic HoB<sub>4</sub> particles provide strong pinning to the vortex lines, together with the considerable reduction in the grain size by addition, leads to the strong improvement of  $J_C(H)$  in the codoped samples.

### 5.5.4 Conclusion of the addition study

The superconducting properties of added MgB<sub>2</sub> differ for the two additives. BRH caused considerable amount of C substitution at B site and formed Mg<sub>2</sub>Si and Mg<sub>2</sub>C<sub>3</sub>. Ho<sub>2</sub>O<sub>3</sub> decomposed and reacted with B to form HoB<sub>4</sub>.



Table 5.15: Influence of different categories of additives on MgB<sub>2</sub>.

Additive	Enhancement of $J_C(H)$	Main reason for $J_C(H)$ enhancement
Nano REO	marginal	Pinning by reaction induced impurities (REB <sub>4</sub> , MgO etc)
Nano TiC	moderate	Pinning by unreacted nano TiC inclusions
Nano SiC	Significant	Carbon substitution and pinning by reaction induced inclusions (Mg <sub>2</sub> Si, SiC)
<b>BRH</b>	<b>Significant</b>	Carbon substitution and pinning by reaction induced inclusions (Mg <sub>2</sub> Si, Mg <sub>2</sub> C <sub>3</sub> )

No Ho is substituted at either Mg or B site. Considering the  $J_C(H)$  performance, for monodoping, Ho<sub>2</sub>O<sub>3</sub> improved the  $J_C(H)$  moderately, but BRH improved the  $J_C(H)$  strongly. Codoping of Ho<sub>2</sub>O<sub>3</sub> with BRH is found to be much more effective for the enhancement of  $J_C(H)$  of MgB<sub>2</sub> than the mono doping of any one of these additives. The substitution of C at B site by BRH and the formation of magnetic particles of HoB<sub>4</sub> by Ho<sub>2</sub>O<sub>3</sub> are the reasons for the strong improvement of  $J_C(H)$  in the added samples.

## 5.6 Summary of the chemical additions

Summarizing the chapter, the effect of different categories of additives on the in-field in-field critical current density of MgB<sub>2</sub> superconductor is studied and the in-field critical current density is significantly enhanced by selective additives. Table 5.15 summarizes the influence of different categories of dopants on MgB<sub>2</sub>.

Figure 5.35 shows a comparison of  $J_C(H)$  performance of different addition studies carried out in the present work. The undoped MgB<sub>2</sub> has a very low  $J_C$  value of 100-1000 A/cm<sup>2</sup> for fields > 7 T at 5 K. By the selective chemical addition the value of  $J_C$  is enhanced to  $5 \times 10^3$ - $2 \times 10^4$  A/cm<sup>2</sup> for the same fields and temperature. So that the  $J_C(H)$  enhanced by nearly 50 times compared to the pure MgB<sub>2</sub>. Burned rice husk, a novel additive is introduced into MgB<sub>2</sub>, which improved the in-field critical current density of the material strongly and the improvement is at par with most of the best additives/dopants reported so far. Further, codoping studies of different type of materials suitable for substitution/substitution+reaction/reaction are explored and found to be much

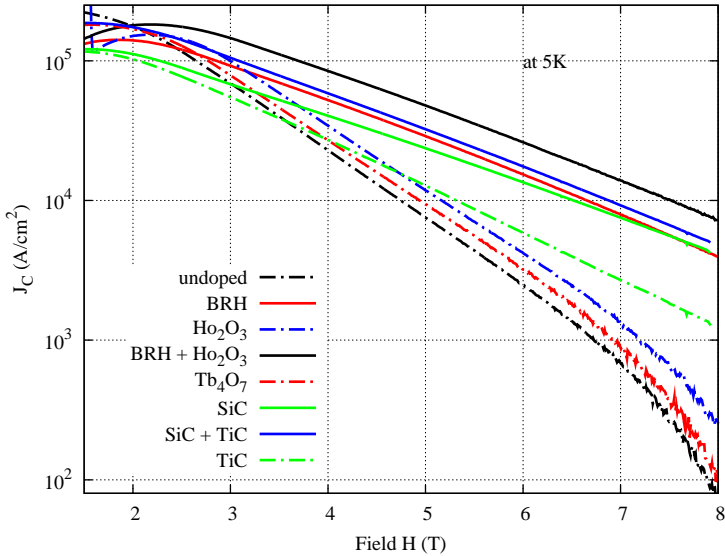


Figure 5.35: Comparison of  $J_C(H)$  performance of  $\text{MgB}_2$  due to different chemical addition. Except BRH, all other additives are commercially available nano materials. The data shown are for addition of 5 wt.% except for codoping where the addition level were 2.5 wt.% for TiC, SiC,  $\text{Ho}_2\text{O}_3$  and 5 wt.% for BRH.

more effective than monodoping. At 5 K and 8 T, the sample added with 5 wt.% of BRH and 2.5 wt.% nano  $\text{Ho}_2\text{O}_3$  has a  $J_C$  of  $0.8 \times 10^4 \text{ A/cm}^2$ , enhanced by 100 times compared to that of the undoped sample. As a conclusion and future direction, it may be fruitful to explore the codoping of more materials with different nature to the  $\text{MgB}_2$  system for better  $J_C(H)$  performance.

# Chapter 6

## Summary and conclusions

### 6.1 Summary of the work

The objectives of the present work were to prepare good quality  $\text{MgB}_2$  superconductor in bulk and wire/tape geometries, and to improve its in-field critical current density by suitable chemical additions.

Good quality  $\text{MgB}_2$  bulk superconductor was successfully prepared by a simple *in situ* Powder-In-Sealed-Tube (PIST) method. In this method, Mg and B powders were filled in seamless stainless steel tubes and heat treated in atmospheric condition after sealing the ends. The method is simple and cost effective, since no vacuum or inert atmosphere is needed for the preparation. For the preparation of wires and tapes a systematic study on the chemical reactivity of various sheath materials such as Ag, Cu, Fe, Ni, SS and Ta with Mg/B was conducted. Among these Fe is found to be the most suitable material for the sheath. Fe sheathed  $\text{MgB}_2$  wires and tapes were prepared by *in situ* Powder-In-Tube (PIT) technique in mono and multi filamentary geometries. Further, a novel electrical self heating method was introduced for the preparation of Fe sheathed  $\text{MgB}_2$  wires and tapes.

The prepared  $\text{MgB}_2$  in bulk, wire and tape forms were characterized for phase purity, crystalline and microstructural properties and superconducting properties. The measured superconducting properties such as  $T_C$ ,  $\Delta T_C$ ,  $J_C$  and  $J_C(H)$  are at par with the best quality samples reported worldwide.

Additives of different types were introduced into the MgB<sub>2</sub> system for improving the in-field critical current density. By selecting suitable combinations of additives a significant enhancement of the critical current density by 1-2 orders of magnitude were achieved for fields > 5 T, at 5 and 15 K.

*Thus the objectives of the work have been achieved. Also most of the results and new findings of the research work included in the thesis are published in SCI journals.*

## 6.2 Conclusions

The main conclusions of the present work are :

1. Standardized a simple and inexpensive method, PIST, for the preparation of good quality MgB<sub>2</sub> bulk superconductors. Typical PIST samples have more than 98% of MgB<sub>2</sub> phase with traces of MgO as the only impurity. The method suppresses Mg loss and Mg oxidation and no vacuum or inert atmosphere is needed for the heat treatment. PIST MgB<sub>2</sub> has sharp superconducting transition with  $T_C$  around 38.5 K and  $\Delta T_C < 1$  K. Critical current densities more than  $10^5$  A/cm<sup>2</sup> at 2 T and 5 K are achieved in typical PIST samples without any additives.
2. Chemical compatibility of commonly used sheath materials such as Ag, Cu, Fe, Ni, SS and Ta with Mg/B at the reaction temperature (600-950 °C) is studied. Among these materials Fe, an inexpensive and easily available material is found to be the most suitable choice for the preparation of *in situ* MgB<sub>2</sub> wires and tapes. Ag, Cu and Ni react with Mg and form impurity phases and reduce the  $J_C$  drastically.
3. MgB<sub>2</sub> wires and tapes in mono and multifilamentary geometries were prepared by the PIT method. For multifilamentary conductors Fe is used as the barrier (sheath surrounding MgB<sub>2</sub>), Cu is used for thermal stabilization and Ni is used as the outer sheath. Ni is selected as the outer sheath since is more resistant to oxidation and more environmentally stable. High thermal and electrical conductivity preferred the choice of Cu as the stabilizer. The prepared MgB<sub>2</sub> conductors have critical temperature in the range 38-39 K. High transport critical current densities in the range  $10^4$ - $10^5$  A/cm<sup>2</sup> at 25-30 K and self-field have been achieved in the wires and tapes.

4. It is demonstrated that  $\text{MgB}_2$  wires and tapes with good superconducting properties can be prepared by a novel cost effective electrical self-heating method.
5. Different categories of additives were introduced into the  $\text{MgB}_2$  for improving its in-field critical current density. The additives include nano rare earth oxides (REO), nano carbides (SiC and TiC) and burned rice husk (BRH).
  - Rare earth oxides react with B to form the respective rare earth boride phase ( $\text{REB}_4$ ) without any lattice substitutions in  $\text{MgB}_2$ . The enhancement of  $J_C(H)$  by REO addition is only marginal, typically 1-2 times.
  - TiC remains unreacted without any lattice substitutions. TiC causes a moderate improvement of 2-5 times in  $J_C(H)$  values at high fields.
  - SiC dissociates and the Si reacts with Mg and forms  $\text{Mg}_2\text{Si}$ . The C released from the SiC substitutes at the B site. As a result, SiC causes significant enhancement of  $J_C(H)$  values at high fields. BRH, a natural material, also results significant enhancements in  $J_C(H)$  values of  $\text{MgB}_2$ . Compared to the undoped sample, nano SiC and BRH added samples have 10-70 times higher  $J_C(H)$  values at higher applied fields.
6. Burned rice husk (BRH), an inexpensive and easy available natural material is found to be effective in enhancing the in-field critical current density of  $\text{MgB}_2$  significantly. The enhancement is comparable to most of the best known additives reported. Thus BRH seems to be a good replacement for the costly nano SiC.
7. Combined addition of both substitution and inclusion type materials produce much more  $J_C(H)$  enhancement than any one type can produce. Two sets of combined additions were studied : first with nano SiC + nano TiC and second with BRH + nano REO ( $\text{Ho}_2\text{O}_3$ ). In both cases samples added with the two additives showed best  $J_C(H)$  values compared to samples added with one of the additives. The sample added with 5 wt.% of BRH and 2.5 wt.% of nano  $\text{Ho}_2\text{O}_3$  have a  $J_C(H)$  of  $0.8 \times 10^4 \text{ A/cm}^2$ , nearly 100 times that of the undoped sample ( $0.8 \times 10^2 \text{ A/cm}^2$ ), at 8 T and 5 K.

### 6.3 Future directions

The present research work reports development of different methods to prepare good quality  $\text{MgB}_2$  superconductor in various forms with improved superconducting properties. However, there are many issues to be addressed before taking these products for practical applications. For the wires and tapes, the heat treatment temperature, duration, starting composition, starting packing density and rolling parameters etc are yet to be precisely optimized and a thorough optimization study is essential for maximizing the current carrying capacity of the conductors. The presented transport current characteristics of the wires and tapes were done only on short length samples of length  $\leq 11$  cm. Whole length transport characteristics in coil form of long conductors are needed for practical applications.

The current transfer problem in multifilamentary conductors has to be minimized and more research work is needed to solve the issue. Another important area that requires considerable applied research is on the thermal stability of the multifilamentary composites. In the present work the prepared multifilamentary conductors have only  $\sim 10\%$  of  $\text{MgB}_2$  area fraction and  $\sim 8\%$  of Cu area. The rest of the composite have materials with low thermal and electrical conductivities. The distribution and size (relative cross sectional area) of  $\text{MgB}_2$ , Cu, Fe and Ni must be optimized for improving the thermal stability of the composite.

Regarding the  $J_C(H)$  improvement, the results presented in the thesis shows significant enhancement by the BRH addition. The raw rice husk contains some organic volatiles, carbon and silica mostly in amorphous form. For the addition purpose this raw rice husk is burned at  $300^\circ\text{C}$  for 1 hour. No chemical or other thermal treatment is done on the raw rice husk in the present study. Heat treatment of the raw rice husk at different temperatures and duration and or chemical treatment of the raw rice husk can be explored for maximizing C and Si and minimizing  $\text{O}_2$  and also for finding the optimum levels of C substitution for the best  $J_C(H)$  behavior. Regarding the new additives Carbides and Borides may be of worth full for investigation. Exploring new inexpensive natural materials also must be continued. Exploration of selective additives in the codoping condition must be fruitful for further improvement of the  $J_C(H)$  of  $\text{MgB}_2$  superconductor.

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