3.1 Preparation of MgB$_2$ samples

In the present work, MgB$_2$ superconducting samples were prepared in bulk and wire forms. *In situ* solid state preparation method was used for both MgB$_2$ bulk and wires [1-3]. Mg powder (-325 #, <50 µm, 99.8 %, Good Fellow) and amorphous B powder (-325 #, <50 µm, 99 %, Merck) were used for all type of preparative methods. Synthesis of bulk samples was done using Powder In Sealed Tube (PIST) method whereas the wire samples were prepared by Powder In Tube (PIT) method. Detailed description of each method is given in coming sections.

3.1.1 Bulk MgB$_2$

Bulk MgB$_2$ polycrystalline samples were prepared using an *in situ* solid state synthesis method, namely Powder In Sealed Tube (PIST) [4, 5]. A schematic diagram of preparation procedure for PIST method is shown in figure 3.1. Stainless steel (SUS 304) tubes were used as the container for synthesis. One end of the tube was pressed uniaxially using a hydraulic press (Herzog TP 20P) so that it became tape shaped. Stoichiometric weights of magnesium and boron powders were taken using an electronic balance (Mettler AE240). The powders were mixed and ground thoroughly in air for about 0.5 hrs to get homogeneous fine powder using an agate mortar and pestle. Then the powder mixture was densely packed through the open end of the pressed SS tube leaving some space unfilled. The unfilled portion was pressed such that both the pressed ends are of equal length. Subsequently, the powder filled middle area was again subjected to uniaxial pressing to get a bar shaped portion. End sealing was performed by arc welding in order to avoid the escape of volatile Mg vapour during the heat treatment. A wet cloth was wound around the specimen during welding to avoid heating up of the sample. The samples were then heat treated directly.
in air at 600-900 °C for appropriate durations with a ramp rate of 5 °C/min and subsequently allowed furnace cooling. Heat treatment of all the samples was done in a programmable muffle furnace having stability and accuracy better than 1 °C, controlled using a temperature controller (Eurotherm 2404). Bar shaped MgB₂ core was taken out by grinding the edges of the samples and then mechanically peeling off the SS sheath for structural and superconducting characterizations.

3.1.2 Preparation of MgB₂ conductors

3.1.2.1 Monofilamentary wires

MgB₂ monofilamentary wires have been fabricated by the conventional PIT method [6-8]. Fe tubes (OD/ID = 5/3 mm) of length 5 cm were used for the preparation of short length monofilamentary wires for regular measurements. For the fabrication of multifilamentary wires, coils and current leads, Fe tubes (OD/ID = 8/6 mm) of length 10 cm were used. The tubes were filled with homogeneously mixed Mg and B powders and then mechanically compacted. The ends of the tubes were sealed by inserting copper studs and further crimped mechanically. The composite tubes were groove rolled down to desired dimensions without any intermediate annealing. The regular wires prepared had a diameter of 1.2-1.8 mm. The ends of the wires were pressed and then welded. Some of the
wires were heat treated by electrical self-heating (described in section: 5.8) and others in a muffle furnace at 550-850 °C for 0.5-2 hrs with a ramp rate of 10 °C/min followed by furnace cooling. After heat treatment, short length samples were cut for various structural and superconducting characterizations. A flowchart of preparation procedure for the fabrication of MgB$_2$ conductors is given in figure 3.2.

![Flowchart of preparation procedure of MgB$_2$ conductors](image)

**Figure 3.2**: Flowchart shows the preparation procedure of mono and multifilamentary MgB$_2$ wires, coils and current leads

### 3.1.2.2 Multifilamentary wires

To prepare multifilamentary wires, the groove rolled monofilamentary wires were cut, bundled and packed inside Ni tubes (OD/ID = 8/6 mm) of length 10 cm. Cu wires of diameter 1 mm were also bundled inside the Ni tube along with the filaments. In the present work, multifilamentary MgB$_2$ conductors were prepared using Fe as inner sheath,
Cu as stabilizer and Ni as outer sheath [9]. Cu is used as the thermal stabilizer, since it has high thermal and electrical conductivity. Ni is chosen as the outer sheath due to its high oxidation resistance at high temperature heat treatment and favorable mechanical properties. The composite was then groove rolled and further heat treated as in the case of monofilamentary wires.

### 3.1.2.3 MgB$_2$ coils

The development of long length multifilamentary wires has enabled the design and fabrication of MgB$_2$ wound solenoid coils. The characterization of these coils gives information on the whole length superconducting properties of MgB$_2$ multifilamentary wires. In the present work, long multifilamentary wires up to a length of 3 m were prepared using MgB$_2$/Fe/Cu/Ni (diameter = 1.65 mm) composite. These wires were then wound and reacted to form coils. The coils were further coated with an insulating layer of styecast. The detailed descriptions of the wires and coils are discussed in chapter 6.

### 3.1.2.4 MgB$_2$ current leads

The MgB$_2$ based current lead is fabricated by PIT technique followed by Wire In Tube (WIT) method. The methodology adopted for the development of MgB$_2$ based current leads is shown in the flowchart (figure 3.2). Stabilized multifilamentary MgB$_2$ superconducting wires are the primary components for these leads. Current leads (MgB$_2$/Fe/Cu/Ni) of around 10 cm length and 5 mm diameter were fabricated from mono wires as test current leads. Detailed description of the current lead fabrication is given in chapter 6.

### 3.2 Structural characterization methods

#### 3.2.1 X-ray diffraction (XRD) analysis

The X-ray powder diffraction technique is the most convenient and easy method for the phase identification of crystalline materials. This technique has been widely employed to examine the phase formation, lattice parameters, strain and grain size. XRD data can also be used for a semi-quantitative phase analysis.
In the present study, powder XRD patterns of the samples were taken using a Philips X’pert Pro (PW 3040/60) X-ray diffractometer with CuKα (λ = 1.540566 Å) radiation employing a proprietary detector viz. X’Celerator and a monochromator at the diffracted beam side. The system has θ-θ Bragg-Brentano geometry with fully automated operation and data acquisition. Programmable slits were used to limit the X-ray beam to the specified sample area. Most of the scans were performed under a tube voltage and current of 40 kV and 30 mA, respectively. The samples were scanned from 20° to 80° (2θ values) with a step size of <0.02°. A typical scan takes about 20 minutes. The samples, either bulk or core of wire, were ground thoroughly into fine powder. The powder samples were then filled in standard sample holders and the XRD data were recorded at ambient conditions. For less amount of powder (especially from wires of smaller diameter) a standard zero background holder was used.

The recorded XRD data were then analyzed for phase identification and lattice parameter calculations. Phase identification of the samples was performed using X’Pert Highscore software with the support of ICDD PDF II database. The volume percentage of different phases in the samples was 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 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 full width at half maximum (FWHM) of an XRD peak depends on factors like crystalline size, lattice strain, instrumental parameters etc. The FWHM of selected peaks of MgB\(_2\) were used for qualitatively assessing the lattice strain and grain size. The analysis of Williamson-Hall plot (FWHM×cosθ against sinθ) was done to estimate the lattice strain and crystallite size from the slope and the y-intercept, respectively [10].
3.2.2 Microstructural characterization methods

The optical images of the cross section of MgB₂ wires were taken using an optical microscope. Grain morphology and microstructure have been examined by a scanning electron microscope (SEM) and a high resolution transmission electron microscope (HRTEM) equipped with energy dispersive spectroscopy (EDS).

3.2.2.1 Optical microscopy

Optical microscopy is used to analyze the cross section of the mono/multifilamentary wires. The cross sectional analysis provides the details regarding core area, homogeneity of the filaments, final geometry and the interface between core and sheath for the mono/multifilamentary conductors. An OLYMPUS SZ-PT model stereo microscope was used for the study and the samples were examined under magnification up to 30X. 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 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.

3.2.2.2 Scanning electron microscopy (SEM)

The scanning electron microscope uses electrons rather than light to form image. Usually it is used to observe the features that are beyond the resolution of the human eye (~100 μm). The combination of higher magnification, larger depth of focus, greater resolution and ease of sample observation makes the SEM one of the most heavily used material characterization techniques today. SEM is normally used to analyze the microstructural properties of materials such as phase formation, precipitations, porosity, shape/orientation of grains, grain size, grain boundary, texture and defects. In the present study, the microstructural analysis was done using a JEOL JSM 5600LV scanning electron microscope equipped with an energy dispersive X-ray spectrometer (Phoenix) used in secondary electron imaging (SEI) mode. The typical images were magnified up to 5000 and 10000 times. The instrument used in this study can magnify images to about 100 nm. Freshly fractured surfaces
of the samples were mounted on brass studs using adhesive carbon tapes. Polished surfaces were also used for some samples especially for wire/tape cross sectional analysis. Since the superconducting MgB$_2$ is electrically conducting, gold coating was not required. Finally, the brass studs with the mounted samples were loaded on the sample holder of the microscope.

3.2.2.3 Transmission electron microscopy (TEM)

TEM permits a direct observation and characterization of fine microstructure. Compared with SEM, TEM has a higher resolution (0.2 nm), which enables the microstructures to be observed in more detail. Besides grain morphology, electron diffraction pattern can be used to obtain precise informations regarding crystal structure, defects and lattice. In this study, TEM is mainly used to get intra and intergrain features of polycrystalline MgB$_2$ and to determine the grain morphology, grain size and informations of the nano sized dopants. The instrument used was HRTEM FEI-Tecnai G$^2$ 30 S-Twin 300 KV equipped with an X-ray energy dispersive spectrometer (EDS). Samples were finely powdered, ultrasonicated in acetone to remove agglomeration and then pipetted on carbon coated copper grids and finally loaded on the device. In the present work, energy dispersive X-ray (EDX) analysis was also done using automated EDS system integrated either to SEM or to TEM. The analysis was done at either single point or area of frame, depending on the requirement. The limitation of EDS in the present study was its inability to accurately detect boron in MgB$_2$ because of its low atomic weight.

3.3 Techniques used for superconducting characterization

The superconducting properties of MgB$_2$ have been investigated by measuring their transport and magnetic properties in self and applied magnetic fields. The superconducting parameters such as $T_c$, $J_c$, $J_c(H)$ and $H_{irr}$ were measured using both magnetization and transport measurements to study the electromagnetic properties of MgB$_2$ samples prepared at different conditions. DC magnetization measurements up to 8 T were done using PPMS (Physical Property Measurement System), in collaboration with RRCAT (Raja Ramanna Centre for Advanced Technology, Indore) and JNCASR (Jawaharlal Nehru Centre for Advanced Science and Research,
Bangalore). An indigenously designed cryostat integrated with helium based cryocooler was used for self-field transport measurements and an 8 T LHe cooled solenoid magnet was used for field transport measurements. Bulk samples were used for magnetization measurements whereas short length wire samples were used for transport currents at high fields.

3.3.1 Magnetization measurements

High field magnetization measurements for the present study were done using a VSM (Vibrating Sample Magnetometer) and SQUID based PPMS in collaboration with RRCAT and JNCASR, respectively. Bulk samples of typical dimensions 3×3×1.5 mm were used for the measurements. The measurements were done with magnetic field applied along the longest dimension of the samples. \( M-T \) (magnetization vs. temperature) measurements were done at 25 or 100 Oe, mainly in zero field cooling (ZFC) condition. \( M-H \) (magnetization vs. field) hysteresis loops were measured at 5 K up to 8 T. \( T_C \) of the sample is defined as the temperature at which the \( M-T \) plot exhibits the onset of diamagnetic property. \( \Delta T_C \) is taken as the difference between the temperatures corresponding to 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 emu/cm\(^3\)) is the width of the \( M-H \) loop, a and b (in cm) are the dimensions (\( a<b \)) perpendicular to the field, for a parallelepiped shaped sample [11]. \( H_{irr} \) values of selected samples were estimated as the field at which \( J_C \) falls below 100 A/cm\(^2\).

3.3.2 Transport measurements

Figure 3.3 shows a schematic sketch of the self and in-field transport measurements of MgB\(_2\) wire samples using four probe resistivity method. For self-field transport measurements, an indigenously designed cryostat integrated with an imported cryocooler is used.
Figure 3.3: Schematic representation of self and in-field transport measurements of MgB$_2$ wire samples using four probe resistivity method

Figure 3.4 shows the schematic sketch of the cryocooler integrated cryostat. The cryocooler used is a Gifford-McMohan cooler manufactured by *Sumitomo Heavy Industries Ltd (SRDK-408)*. For transport measurements, MgB$_2$ wires of 6 cm length were anchored to a home made sample holder placed at the second stage of the cryocooler, where temperature can be lowered down to 6 K. Four probe resistivity method is used for the transport measurements (*figure 3.3*). Oxygen free high conductivity (OFHC) copper wires of suitable gauges were used for both current and voltage measurements. The end leads were directly soldered to the wire sample using ortho phosphoric acid as a flux, after thoroughly cleaning the sheath surface. The in-field transport measurements were carried out by using LHe based 8 T solenoid magnet system (*8 T – 77 mm bore superconducting magnet with J$_c$-VTI, model A8030-3*) manufactured by *American Magnetics Inc. (AMI)*. *Figure 3.5* shows the magnet system comprising the superconducting magnet, variable temperature insert (VTI)
with helium vapor cooled current leads and liquid helium dewar. Samples can be inserted into the uniform magnetic field zone through the top of the dewar. A programmable milli ampere source (Keithley 220/6220) and nano voltmeter (Keithley 181/2182A) were used for Resistance-Temperature (R-T) measurements. Generally, a current of 100 mA was used for the R-T measurements. For Current-Voltage (I-V) measurements programmable current sources of capacity 100 A (APLAB 9711 P) and 1000 A (Sorensen DHP 5-1000 M1M9D) were used. The R-T and I-V measurements were automated and controlled by a PC, interfaced with the system through GPIB/LABVIEW. Lakeshore L332/L340 model temperature controllers were used for monitoring and controlling the sample temperatures.

Resistance-Temperature and Current-Voltage characteristics of the samples were used to determine the $T_C$ and $I_C$ of the samples, respectively. 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 is defined as $\Delta T_C$ for the samples. During I-V measurements, a ramping current was passed for short durations (10-100 ms) at regular intervals of time. 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 cross sectional area of MgB$_2$ core is taken as the critical current density ($J_C$). $J_C(H)$ and flux pinning force were calculated from the measurement of transport $I_C$ at different magnetic fields.
Figure 3.4: Schematic diagram of cryocooler integrated cryostat

1. SRDK 4085 cold head
2. Current feed through
3. Pirani sensor
4. 12 mm thick door
5. Sample holder
6. Vacuum chamber
7. Vent valve
8. Thermal shield
9. Isolation valve
10. Rotary vacuum pump
11. Support frame
12. Caster wheel
Figure 3.5: LHe based 8 T high field solenoid magnet system
References:


