

Phase formation of superconducting MgB₂ at ambient pressure

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Abstract. MgB₂ superconductor has been synthesized using a simple technique at ambient pressure. The synthesis was carried out in helium atmosphere over a wide range of temperatures. Magnesium was employed in excess to the stoichiometry to prevent the decomposition of MgB₂. Samples of MgB₂ thus prepared have been almost free from MgO as compared to other methods. Resistivities of the samples are quite low with residual resistivity ratio (RRR) of around 3. $T_c(R=0)$ is 38.2–38.5 K with ΔT_c of 0.6–1.0 K. Comparative studies of various methods of low pressure synthesis have been presented.

Keywords. MgB₂; low-pressure synthesis; superconductivity.

1. Introduction

The discovery of superconductivity in magnesium diboride (MgB₂) (Nagamatsu *et al* 2001) at around 40K has attracted a lot of attention because of its wide advantages as compared to high T_c cuprate superconductors. The room temperature conductivity in this system is fairly high. It is a simple binary intermetallic system with hexagonal crystal structure. Considerable efforts have been put on the synthesis of samples in the form of bulk pellet, tape, thin film and wire. Bulk samples are in general prepared by direct reaction of magnesium (Mg) and boron (B) powder involving high-pressure and high temperatures (Dhalle *et al* 2001; Yu *et al* 2001), which are not commercially viable. Low pressure synthesis is done usually in inert atmosphere of flowing argon (Podder *et al* 2003). But, there are chances of magnesium being expelled by argon and thereby the formation of MgB₂ might not be complete. MgB₂ is often accompanied with the formation of MgO due to vigorous reaction of magnesium with oxygen. There are also attempts to synthesize in vacuum (Feng *et al* 2002). But, MgB₂ under vacuum is prone to decomposition (Liu *et al* 2001). We have undertaken the synthesis of MgB₂ at ambient pressure from Mg and B, but in a sealed atmosphere of helium to ensure the inert atmosphere. This would also eliminate the escape of magnesium from reaction front. The method is quite simple and assures the formation of single phase of MgB₂ with low room temperature resistivity.

2. Experimental

For preparation of bulk samples, mixture of Mg and B (> 99% pure) powders were taken with 2 at.% of Mg in

excess to the stoichiometry and was thoroughly ground for uniformity. Excess Mg was employed to compensate for the loss of volatile magnesium. The mixture was pelletized by applying uniaxial pressure of 7500 kg/cm². The pellets were wrapped in tantalum foil, put in quartz tubes and evacuated to 10⁻² torr. They were purged with 99.9% pure helium quite a number of times and sealed in helium environment (at ~ 800 torr). The inert gas environment of helium was required to avoid the formation of MgO phase. The samples were given following heat treatments: (a) 750°C for 2 h, then 800°C for 1 h and quenching at 625°C, (b) 800°C for 2 h, then 900°C for 1 h and quenching at 650°C, (c) treatment as in (b) but the samples were furnace cooled, (d) treatment as in (b) but without wrapping the sample in tantalum. Samples thus prepared are henceforth indicated as A, B, C and D, respectively. Quenching of samples was done with the idea of arresting the phase formed after the heat treatment. The sample in process (c) was furnace cooled to see the difference from quenching. The quartz tube in preparing the sample D cracked. This was due to enormous heat release from the exothermic reaction during the formation of MgB₂ from its constituent elements. Hence an inert metal like tantalum was required to act as heat sink.

The samples thus prepared were characterized by X-ray diffraction pattern taken with Philips PW1710 diffractometer with Cu K α of wavelength 1.54 Å. Resistivities as function of temperature for the samples were measured in close cycle helium refrigerator (make, Cryoindustries of America Ltd.) using four-probe technique with HP 34220A Nanovoltmeter with a resolution of 0.1 nanovolt and Keithley Programmable Constant Current source 224. 1 mA current was employed for extraction of T_c . The values of T_c , RRR (i.e. the ratio of resistivity at room temperature to that at T_c onset) and residual resistivity, r_0 , are listed in table 1.

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3. Results and discussion

Figure 1 shows X-ray diffraction patterns of the samples A to D. From XRD patterns, we see that for the samples A, B and C, MgB₂ phase formed almost quantitatively along with trace of MgO. For the sample D, significant amount of MgO had formed. The lattice parameters (*c* and *a*) for the samples A, B and D presented in table 1 obtained from Rietveld analysis using LS1 programme are in close

agreement with the values obtained for MgB₂ (Nagamatsu *et al* 2001). The lattice parameters as well as angles (*a*, *b*, *g*) were obtained as fitted parameters. XRD patterns of A, B and C are similar showing thereby that there is no difference in phases formed due to quenching and furnace cooling.

Resistivity vs temperature plots for samples A and B as representatives are shown in figures 2a and b. The residual resistivity ratios (RRR) for samples A, B and D

Table 1. The lattice parameters and crystallographic angles of the samples A, B and D.

Sample	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>a</i> (degree)	<i>b</i> (degree)	<i>g</i> (degree)
A	3.0902	3.0902	3.5299	90.270	89.944	119.97
B	3.1016	3.1016	3.5413	90.309	89.749	120.10
D	3.0768	3.0768	3.5163	90.358	90.046	120.41

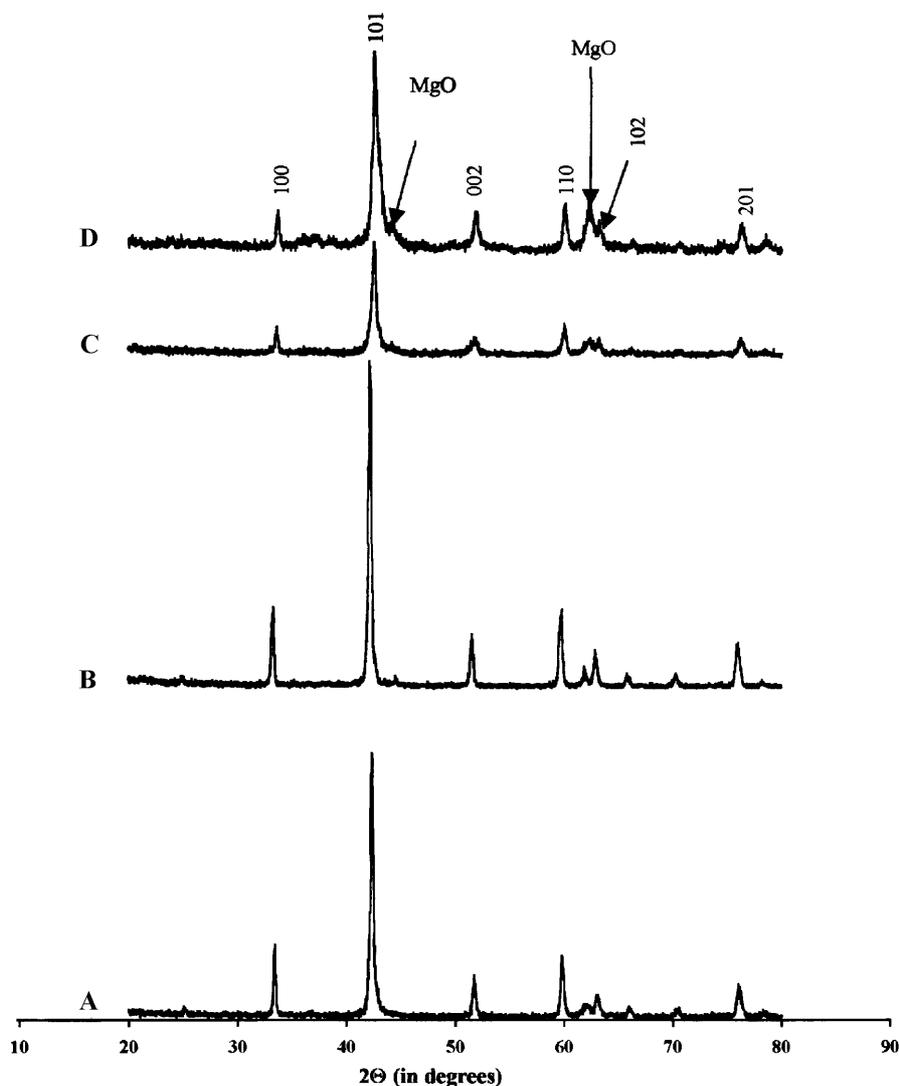


Figure 1. XRD patterns of the samples A, B, C and D.

presented in table 2 are between 2.4 and 3.3. RRR within 2–3 are generally observed in the polycrystalline samples. The low RRR may be due to the quality of boron (Podder *et al* 2003). The room temperature resistivities, r_{300} , for samples A and B are about 94 $\mu\text{-ohm cm}$ and 84 $\mu\text{-ohm cm}$, respectively and for sample D about 796 $\mu\text{-ohm cm}$.

The prepared samples A, B and C showed formation of MgB₂ with trace of Mg and MgO as impurities. Formation of MgO was higher in case of sample D, which is due to the fact that cracking of quartz tube exposed the sample to air and hence the unreacted Mg reacted with oxygen of air. The r_0 and r_{300} values obtained from resistivity measurement are also higher (~ 10 times) than other samples. The higher r_0 and r_{300} values were due to the formation of MgO which being an insulator reduced the conductivity of MgB₂.

Synthesis of MgB₂ under flowing argon leads to the formation of MgO in large amount. This is because of

oxygen in air, which is admixed with argon. We have undertaken a thermogravimetric analysis (TGA) of Mg and B mixture in flowing argon up to 800°C—the temperature employed for the preparation of MgB₂ in flowing Argon. The thermogram in figure 3 shows a distinct increase in weight from around 450°C which is due to the formation of MgO. Hence comes the need of preliminary evacuation followed by repeated purging in helium, adopted by us. This guarantees the minimization of oxygen. Above 750°C, there is a decrease in weight, which might be due to loss of magnesium from reaction mixture as it becomes volatile at that high temperature. We have carried out the synthesis in helium environment in sealed condition, whereby magnesium remains in intimate contact with the reaction mixture.

From the phase diagram study of Mg and B (Liu *et al* 2001), it is seen that MgB₂ has low thermal stability at lower magnesium vapour pressure of about 10^{-2} torr where

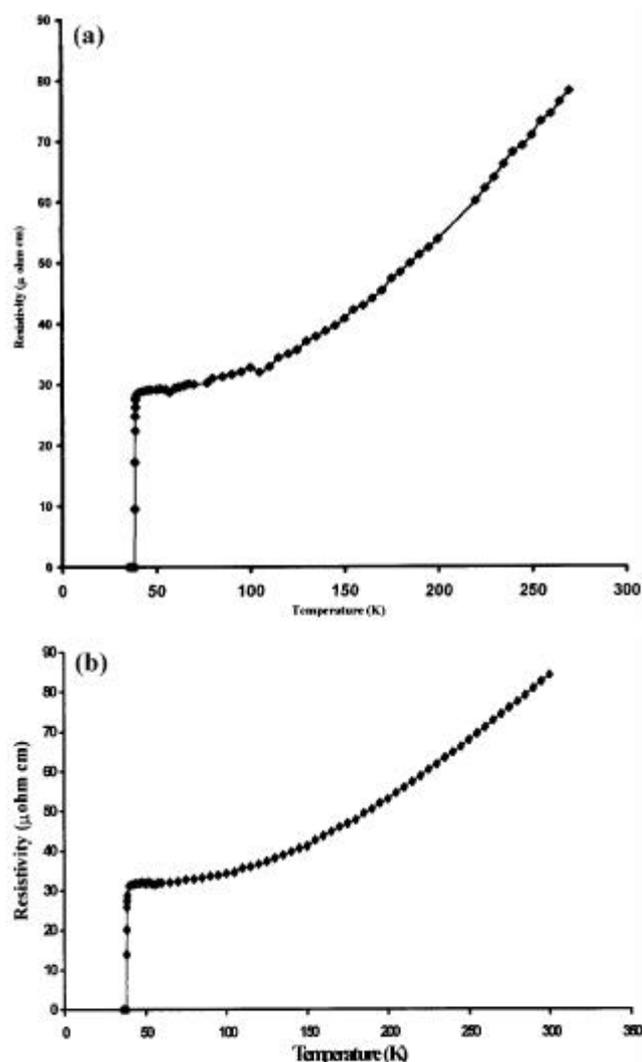


Figure 2. Temperature dependence of resistivity of sample A prepared at (a) 750–800°C and (b) 800–900°C.

Table 2. Values of critical temperature, transition width, residual resistivity, room temperature resistivity and residual resistivity ratio for the samples A, B and D.

Sample	T_c (K)	ΔT_c (K)	r_0 ($\mu\Omega\text{-cm}$)	r_{300} ($\mu\Omega\text{-cm}$)	RRR
A	38.5	0.6	28.58	94.434	3.3
B	38.4	1.0	31.18	84.353	2.71
D	38.2	0.6	320.32	796.598	2.49

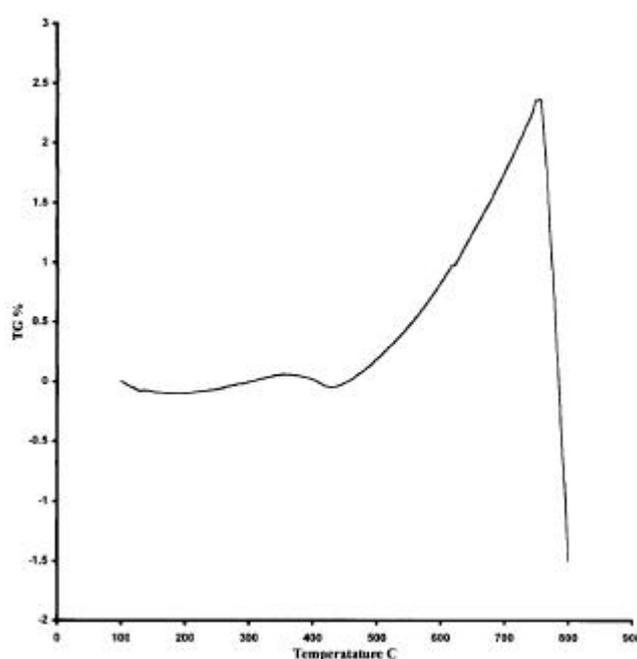


Figure 3. Thermogram of Mg and B mixture in argon flow. TG value expressed as % shows the change in weight of the sample normalized with respect to initial sample weight.

it seems to decompose as: $\text{MgB}_2 \rightarrow \text{Mg} + 2\text{B}$. Presence of excess magnesium shifts the equilibrium towards left and thus prevents MgB_2 from decomposition. Also low magnesium content in reaction mixture leads to the formation of phases containing larger amounts of boron like MgB_4 and MgB_7 (Liu *et al* 2001). Hence excess magnesium has to be employed to prevent the decomposition and formation of phases containing larger amounts of boron. We have not observed any trace of Mg in XRD pattern. Hence, if there is any trace of Mg due to its employment in excess, it is likely to occupy grain boundary region and increase the conductivity of the polycrystalline samples. So, it is not harmful to have magnesium along with the formation of MgB_2 .

4. Conclusions

We have undertaken a fairly simple way of synthesis of MgB_2 from magnesium and boron mixture at ambient pressure. The method involves preevacuation followed by purging in helium and then carrying out the reaction in a sealed tube in helium atmosphere. This guarantees the absence of oxygen and ensures intimate contact of Mg and B leading to the formation of MgB_2 . Excess magnesium employed does not degrade superconducting proper-

ties. Phase formation occurred at wide range of temperatures. Since the reaction of Mg and B is highly exothermic, it is advisable to employ an inert metal like tantalum for the dissipation of heat evolved during reaction. Otherwise, there may be cracking of the tube and formation of MgO by exposure of Mg with air.

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