

# Superconductivity in dense $\text{Mg}_{1-x}\text{M}_x\text{B}_2$ ( $\text{M} = \text{Zr, Nb, Mo}$ ; $x = 0.05$ ) materials sintered under pressure

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**Abstract.** Dense compacts of superconducting  $\text{MgB}_2$  material have been produced by sintering under 3 GPa pressure and 900°C using a cubic anvil apparatus. The starting material was produced by the powder in tube (PIT) method at low pressure and in argon atmosphere. The effect of substitution of Mg sites with non-magnetic 4d-transition metals (Zr, Nb, Mo) on the superconducting transition temperature ( $T_c$ ) has been studied by resistivity and susceptibility measurements. The results indicate that there is a small gradual reduction in the transition temperature as we move from Zr to Mo.

**Keywords.** Magnesium diboride; superconductivity; high pressure; resistivity; susceptibility.

## 1. Introduction

The discovery of superconductivity in  $\text{MgB}_2$  (Nagamatsu *et al* 2001) with a transition temperature ( $T_c$ ) of about 40 K has started a flurry of research activities. This is the first non-oxide superconductor to show such a high  $T_c$ . The  $\text{MgB}_2$  structure (space group  $P6/mmm$ ) consists of a layered stacking with alternate Mg and B layers ( $a = 3.086 \text{ \AA}$  and  $c = 3.524 \text{ \AA}$ ). Following its discovery, measurements on commercial and also laboratory synthesized samples have brought about a wealth of information about this new material. Even though the  $T_c$  is just about the maximum that is predicted by the conventional BCS theory based on the electron–phonon interaction, the data that have come from the plethora of experiments have raised a lot of questions regarding the mechanism of superconductivity in this material.  $\text{MgB}_2$  has shown a number of unique features. For instance, it is characterized by two bands in the Fermi surface (Amy *et al* 2001), anisotropy in upper critical field (Angst *et al* 2002), anisotropy in the superconducting order parameter (Kortus *et al* 2001) and so on. Another intriguing feature is that defying the initial predictions of band theoretical calculations, substitutions both at Mg and B sites have only reduced the  $T_c$ . Substituting Al for Mg has shown a larger decrease (Slusky *et al* 2001) compared to other substitutions at Mg site. Partial substitution of C for B (Bharathi *et al* 2002) has also brought down the transition temperature. Initially pure  $\text{MgB}_2$  samples were synthesized at low pressure and in argon atmosphere to prevent the formation of  $\text{MgO}$ . These samples were porous. Nevertheless they showed very sharp transition ( $\Delta T_c < 1 \text{ K}$ ) to superconducting state

at  $\sim 40 \text{ K}$ . They also showed very high RRR values ranging from 6 to 25 thereby satisfying the Testardi correlation (Buzza and Yamashita 2001) required for very good superconductors. Despite all this the surface degradation of the porous samples results in the broadening of transition though the  $T_c$  itself remains unaffected. Attempts to densify the samples by annealing at ambient pressures and high temperatures were found to be detrimental to superconductivity. This and the requirement to produce dense samples for further metallurgical processes resulted in high pressure sintering and also high pressure – high temperature synthesis (Jung *et al* 2001) of  $\text{MgB}_2$ .

In this paper we present the results of high pressure and high temperature sintering of pristine  $\text{MgB}_2$  and  $\text{M}_{0.05}\text{Mg}_{0.95}\text{B}_2$  ( $\text{M} = \text{Zr, Nb, Mo}$ ) using a cubic multi anvil press. From the literature it is known that substitution of 3% 3d-transition metals in Mg site decrease  $T_c$  (Moritomo and Xu S; Kazakov *et al* 2000). Zn was the only exception which showed a very small increase in  $T_c$ . In this background it is interesting to substitute non magnetic 4d-transition metals and observe their role in the superconductivity of  $\text{MgB}_2$ . We took a novel approach of synthesizing the pristine and substituted samples at low pressure (LP) and sintering them at high pressure (HP) in the cubic anvil apparatus.

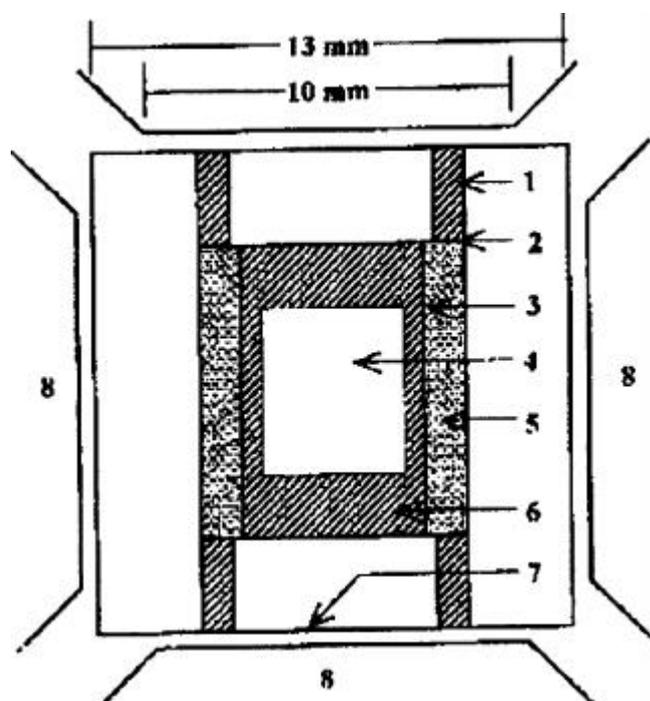
## 2. Experimental

Stoichiometric quantities of Mg (99%), amorphous B (99%) and the 4d-elements (Zr, Nb, Mo (99%)) were weighed, ground, made into pellets and placed in a Ta tube. The Ta tube was kept in a thick walled SS tube fitted with a high pressure valve. After evacuation and flushing with Ar the SS tube was sealed at an Ar pressure of 35

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bar. This assembly was put in a quartz jacket with a Wilson's seal and lowered in a vertical furnace for synthesis at 900°C for 90 min and then furnace cooled. The resulting porous pieces and powder which were black in colour were characterized to be highly phase pure by XRD. The high pressure sintering was carried out in a 200 ton cubic anvil apparatus with an anvil face of 10 mm (Bhaumik *et al* 1996). Direct contact of the sample with the graphite heater was avoided by enveloping the sample in a tantalum foil. The schematic of the high pressure–high temperature cell is shown in figure 1. While maintaining a pressure of 3 GPa, the temperature of the sample was increased to 900°C by passing a current through the graphite heater. The samples recovered after 2 h of sintering were about 3 mm in diameter and 4 mm in height with a mass of 100 mg. They were golden yellow in colour and had a density of 2.5 g/cc.

The X-ray diffraction studies of the pristine and 5% 4*d*-substituted MgB<sub>2</sub> samples were carried out in a STOE diffractometer with CuK<sub>α</sub> radiation. Superconducting transitions were traced by a.c. susceptibility and resistivity techniques from room temperature down to 4 K using a dipstick arrangement in a liquid helium dewar. The susceptibility signal was obtained using a coil assembly with compensated secondary coils. A PAR model 5210 lock-in amplifier was used to record the secondary e.m.f. Four-probe resistivity at room temperature was measured on a

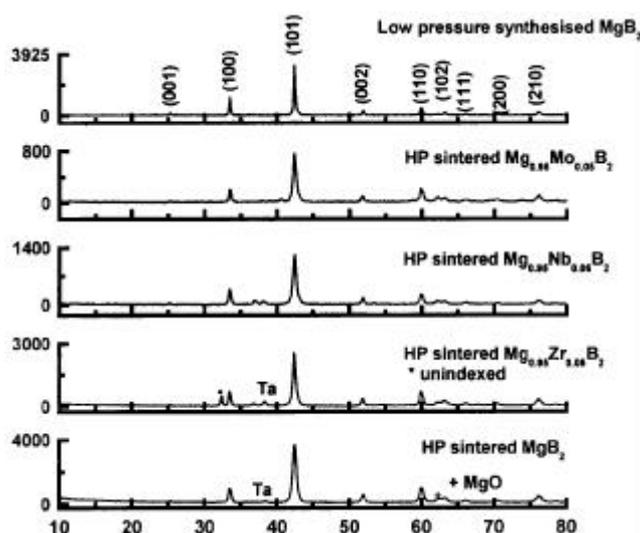


**Figure 1.** The schematic of the high temperature–high pressure cell: 1. Steel current ring, 2. tantalum disc, 3. tantalum liner, 4. sample, 5. graphite heater, 6. graphite plug, 7. tantalum disc, 8. WC anvils and the remaining portions of the cell is pyrophyllite.

thin circular disc sample in the Van der Pauw geometry. Electrical contacts to the 2.5 mm sample discs were made using silver paste. Resistive transitions were recorded by applying a current of 50 mA from a highly stable current source (Time Electronics make) and measuring the voltage developed using a Keithley 181 Nanovolt meter. A Lakeshore make calibrated diode sensor was used to measure the temperature. The error in measured temperature is less than 50 mK. The SEM observations of the porous as well as the sintered pellets were made using a JEOL model JSM 5410 SEM.

### 3. Results and discussion

The results of the XRD studies are shown in figure 2. All the lines characteristic of MgB<sub>2</sub> are present. The structure of MgB<sub>2</sub> is hexagonal with the space group *P6/mmm*. It is to be noted that the LP synthesized sample has almost no trace of MgO since it was prepared in a high purity Argon environment. In the HP sintered samples, it is seen that the 100% peak corresponding to (1 0 1) line of MgB<sub>2</sub> is broadened due to the merging of the (2 0 0) line of MgO at  $2\theta = 42.916^\circ$ . A small peak corresponding to the next higher intensity line (2 2 0) at  $2\theta = 62.3^\circ$  is also present indicating presence of MgO. This could have probably come due to some Mg reacting with O<sub>2</sub> during high pressure sintering where control of the gaseous environment was not possible. No peak corresponding to MgB<sub>4</sub> phase was observed. A small peak corresponding to 100% line of Ta (1 1 0) is present at  $2\theta = 38.47^\circ$ . It is not expected that Ta would have gone into the bulk. A very thin ring of Ta might be adhering to the periphery of the circular disc sample and hence contributing to the observed line. The 4*d*-substituted samples show a small shift in the



**Figure 2.** XRD pattern for low pressure synthesized and high pressure sintered pristine and 5% 4*d*-substituted MgB<sub>2</sub> samples.

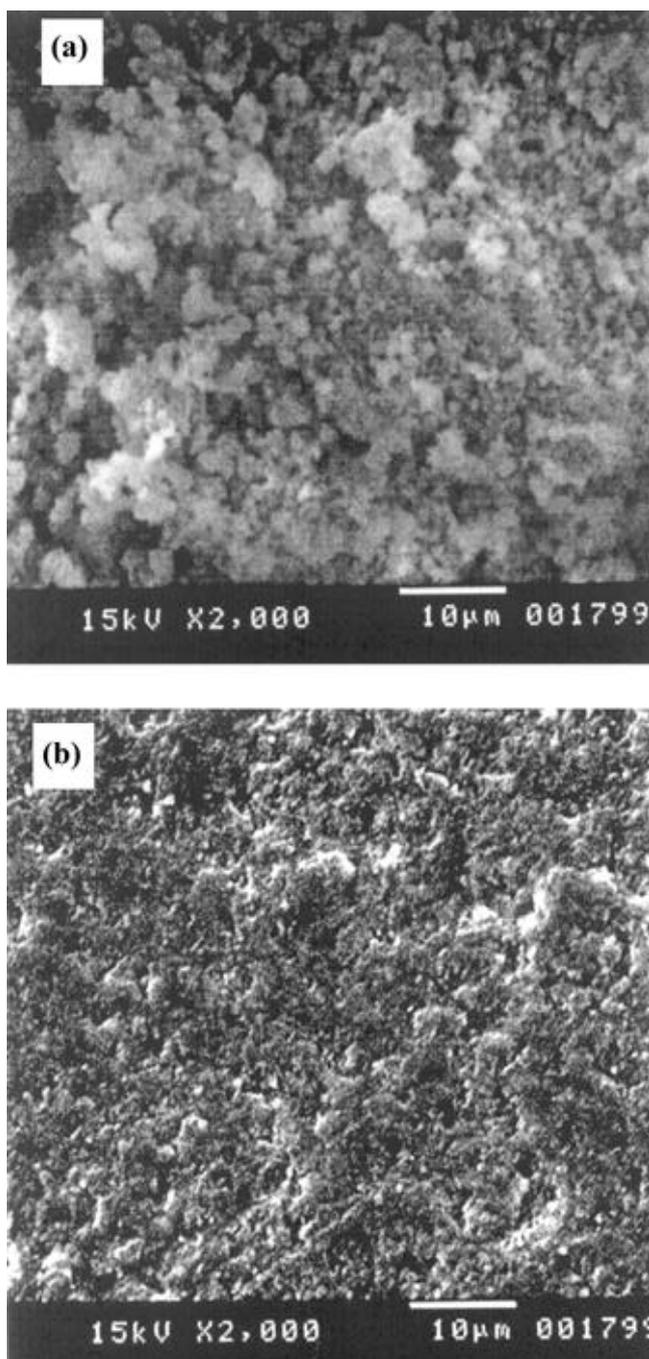
(0 0 2) peak (not shown) with respect to pristine  $MgB_2$ . The  $c$ -lattice parameter (table 1) also shows an increase. This implies substitution of Zr, Nb and Mo at the Mg site. The SEM micrographs (figure 3) of the low pressure synthesized sample and the high pressure sintered sample clearly show the dense nature of the high pressure sintered sample with good grain connectivity. The normalized resistivity plots are presented in figure 4. The superconducting transition ( $T_c$ ) onset is at 40 K for the pristine

$MgB_2$ . It decreases to 39.5 K, 39.3 K and 38.9 K with the substitution of Zr, Nb and Mo, respectively.

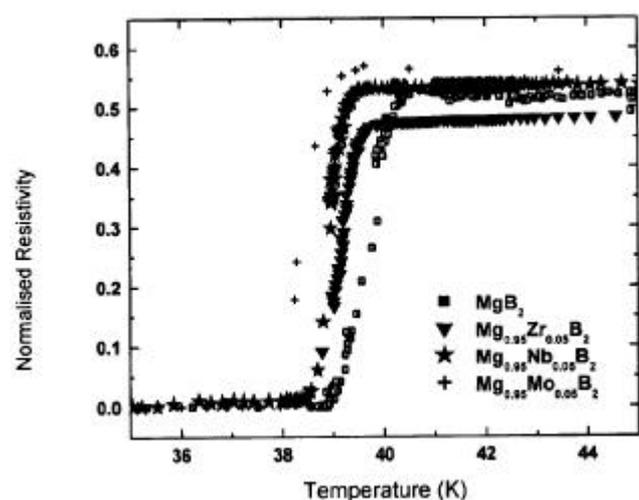
The resistivity ratio between the resistivity at 300 K and that at 40 K (RRR) usually varies from 6 to 25 in most of our low pressure synthesized samples. In the high pressure sintered sample we find a value of RRR = 2. The sample that is chosen for high pressure sintering is one of the earlier samples that we had synthesized at low pressure. The synthesized material was a porous powder and hence resistivity data does not exist for comparison. The resistivity of the pristine  $MgB_2$  sample just above the superconducting transition (40 K) was  $75 \mu\Omega \text{ cm}$ . This value is higher compared to the value quoted in the literature viz.  $60 \mu\Omega \text{ cm}$ . This increase can be attributed to the error in dimensional measurements of the sample and also to the presence of a very small ring of Ta adhering to the peripheral surface of the sample disc.

Figure 5 shows the normalized susceptibility data. When the sample undergoes superconducting transition a negative secondary e.m.f. due to the diamagnetism of the sample is observed. In some of the very good samples, a difference in secondary e.m.f. between the paramagnetic normal state and the diamagnetic superconducting state would be about  $500 \mu\text{V}$  for  $\sim 25 \text{ mg}$  of sample. The sample that is chosen for high pressure sintering showed  $355 \mu\text{V}$ . For easy comparison of the superconducting transition of all the samples the signal strength was normalized to 100%. The  $T_c$  onset corresponding to the pristine  $MgB_2$  is again 40 K and it decreases to 39.65 K, 39.35 K and 39.17 K for Zr, Nb and Mo samples in that order (table 1).

The electronic band structure calculations (An and Pickett 2001; Kortus *et al* 2001) carried out on  $MgB_2$  conclude that  $MgB_2$  being essentially metallic, has boron held together by strong in plane covalent B–B bonding and weak out of plane B–Mg bonding. This is characterized



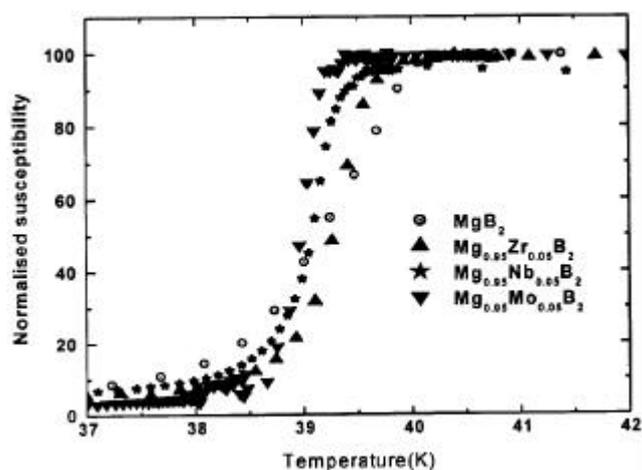
**Figure 3.** SEM corresponding to (a) low pressure synthesized  $MgB_2$  and (b) high pressure sintered  $MgB_2$ .



**Figure 4.** The normalized resistivity,  $R(300)/R(T)$  as a function of temperature. The  $T_c$  onset decreases with the substitution of 5% Zr, Nb and Mo.

**Table 1.** Summary of the results.

No.	Sample	'a' – lattice parameter (Å)	'c' – lattice parameter (Å)	Cell volume (Å) <sup>3</sup>	Susceptibility, T <sub>c</sub> (K)	Resistive, T <sub>c</sub> (K)
1.	MgB <sub>2</sub> – LP synthesized	3.0840(12)	3.5215	29.01	39.75	–
2.	MgB <sub>2</sub> – HP sintered	3.0826(6)	3.5213(8)	28.978	40.00	40.00
3.	Mg <sub>0.95</sub> Zr <sub>0.05</sub> B <sub>2</sub>	3.0837(10)	3.5264(14)	29.040	39.65	39.50
4.	Mg <sub>0.95</sub> Nb <sub>0.05</sub> B <sub>2</sub>	3.0826(6)	3.5244(17)	28.982	39.35	39.30
5.	Mg <sub>0.95</sub> Mo <sub>0.05</sub> B <sub>2</sub>	3.0837(14)	3.5284(20)	29.057	39.17	38.90

**Figure 5.** Normalized susceptibility as a function of temperature for pristine and 5% substitution of Zr, Nb and Mo. The T<sub>c</sub> onset decreases on substitution.

by the existence of hole like cylinders at the  $\Gamma$  points of the Fermi surface. This is due to the in plane,  $p_{xy}$ , boron bands. Mg is fully ionized and the electrons donated to the system are not localized but are distributed over the whole crystal. Hall effect measurements done on polycrystals and  $c$ -axis oriented thin films (Kang *et al* 2001) and films without preferential orientation (Jin *et al* 2001) have all shown a positive Hall coefficient, confirming holes as charge carriers in the normal state. Substitution of Zr, Nb or Mo would increase the filling of  $p_{xy}$  bands (Medvedeva *et al* 2001). This consequently reduces the hole density and could explain the decrease in T<sub>c</sub>.

#### 4. Conclusions

In conclusion, pristine and 5% (Zr, Nb and Mo) substituted MgB<sub>2</sub> samples were synthesized at low pressure (50 bar) and sintered at 3 GPa and 900°C using a cubic multi anvil cell. The samples were dense with a golden yellow lustre. The superconducting properties that deteriorate under ambient pressure sintering, remained in tact after high pressure sintering. Unlike substitution of Al or 3d-metal like Mn, 4d-substitution at Mg site results in a smaller decrease in T<sub>c</sub>. This may be due to a small reduc-

tion in the density of holes which are the majority carriers in MgB<sub>2</sub>.

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