Influence of oxygen doping on critical fields in MgB$_2$ bulk superconductors

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Abstract. In this work we studied the influence of SnO$_2$ doping on the critical fields and temperatures of MgB$_2$ bulk samples. Bulk samples were made by mixing ex-situ MgB$_2$ powder with 5 wt% SnO$_2$ powder and then pressing the mixed powders into pellets using a pressure of 2000 psi. The bulk pellets were sintered at 900°C in a furnace under flowing Ar. The samples were quenched to room temperature after dwelling at 900°C for 5h. XRD, SEM, and magnetic measurements were made on doped and control samples. XRD showed a decomposition of the SnO$_2$ and very slight reductions in the a-axis and c-axis lattice parameters of the MgB$_2$ phase. $M$-$T$ (Magnetization-Temperature) curves showed a decrease in $B_c2$ of approximately 1 T in the temperature range of 24 K - 39 K with SnO$_2$ additions as compared to the control samples.

1. Introduction

MgB$_2$ superconducting materials are of significant interest because of their relatively high critical temperature (~ 39 K), low cost, and simple two-gap nature. MgB$_2$ has strong interest for low to moderate field (0-3 T) applications in the 4-30 K temperature range, including MRI [1,2], superconducting motors and generators [3,4], and fault current limiters [5]. However, high field applications are limited by its relatively low upper critical field ($B_{c2}$) and low irreversible field ($B_{irr}$) which leads to low critical current densities ($J_c$) at high magnetic fields as compared to Nb$_3$Sn or YBCO. Much research has focused on the chemical doping of MgB$_2$ aimed at increasing either critical fields, critical currents, or both [6-13]. The most successful dopant has been C, added directly or as a compound, which releases C during reaction, which increases $B_{c2}$ [12-13]. A few other dopants have been investigated which may add small amounts of flux pinning [14-15], but the increases in $J_c$ were marginal since most dopants (except C) tend to segregate at grain boundaries. Some promising work on Dy$_2$O$_3$ has shown increases in $J_c$, although the mechanism is not fully clear [16-19]. However, a certain level of nanoscale intragrain defects were observed [17] in Dy$_2$O$_3$ doped MgB$_2$. In any case, the critical field increases seen in bulk and wire samples, while significant, have not reached the levels seen in earlier doped thin film work where critical fields of around 60 T and higher were seen at 4.2 K [7,8]. Oxygen doping appears to be part of the mechanism for the critical field increases seen in thin films, but so far, such increases have not been substantially translated to wires or bulks. Dou et al [6] used Sb$_2$O$_3$ powders as additions to in-situ route MgB$_2$ in an attempt to increase the critical fields, and in fact modest increases (about 1.3 T at 23.75 K) were seen in $B_{c2}$. In this work, we attempt to dope bulk samples with oxygen by including a SnO$_2$ powder additive to MgB$_2$ ex-situ powders. SnO$_2$ is an oxide which becomes unstable above 500°C, and thus we will use this as a dopant in an attempt to provide an internal oxidation source for our MgB$_2$ ex-situ powder samples. We chose SnO$_2$ not only because of its above-noted decomposition, but also because Sn additions have been shown to be relatively benign additions to MgB$_2$ [20-21]. Below we carry out an initial study which attempts to increase the critical fields via oxygen doping using SnO$_2$ as the carrier.
2. Experimental details

Two MgB₂ samples were prepared using ex-situ powders which were pressed into pellets and then heat treated. One was made using pure pre-reacted MgB₂ powders (99% pure). A second, doped sample used pre-reacted MgB₂ powders (99% pure) mixed with 5wt% SnO₂ powders (99% pure) in order to investigate the influence of SnO₂ additions on the critical fields of MgB₂ bulks. First, the powders were mixed. Then the mixed powders were pressed into pellets (8.8 mm OD and 5 mm in height) under a load of 2000 psi at room temperature. The pellets were then sintered. The temperature was ramped up at 5°C/h, then held at 900°C under flowing Ar, and then the sample holder was pulled directly out of the furnace.

Microstructures of the MgB₂ pellets (after powderization) were characterized by scanning electron microscopy (SEM) using an FEI Sirion FEG in secondary mode. Powder X-ray diffraction (XRD) was performed using a Rigaku MiniFlex 600. XRD patterns were collected from 20 degrees to 80 degrees with a rate of 0.02 degree/step. The phases in the materials were identified, and lattice parameters were obtained for the MgB₂ phase.

Magnetization-Temperature (M-T) curves were measured on the samples from 5 K to 45 K using the vibrating sample magnetometer (VSM) mode of a Quantum Design Physical Property Measurement System (PPMS). In order to perform the measurements, the sample was first taken above Tc, a field of 0 T was applied, and the sample was cooled in zero field to 5 K. A field of 0.1 to 5 T was then applied, and the temperature slowly increased (5 K/h) until 45 K was reached; this constituted the zero field cooled measurement (ZFC). Once 45 K was reached, the field was left on while the temperature was again decreased through the transition and finally to 5 K; this was the field cooled (FC) measurement. The critical temperature at a given field was defined to be the point at which the deviation from the normal state magnetization (taken as a fraction of the total magnetization change during the ZFC measurement) was 5%. The irreversibility temperature was defined as the point at which the ZFC and FC measurements at a given field diverged [22]. Since Tc (TIR) at a given field can be interpreted as Bz₂ (Bz2) at a given temperature, these results are presented as Bz₂ and Bz2 vs T below.

3. Results and Discussions

3.1. Microstructure of the MgB₂ pellets

Figure 1 shows the SEM (secondary electron, SE mode) of the undoped sample (left) and the SE-SEM of the 5wt% SnO₂ doped sample (right). Both samples have been ground into fine powder, after which the powder was coated with a layer of gold for the SEM since there was charging effect due to bad connectivity in the samples. The grains are roughly equiaxed and SnO₂ additions did not make an appreciable change in the sample morphology. Furthermore, no noticeable secondary phases were seen from SEM images.

![Figure 1 SEM images of undoped MgB₂ bulk sample (a) and the SnO₂ doped MgB₂ bulk sample (b). Pellet samples were powderized and gold coated before SEM.](image-url)
3.2. Structure and phase analysis

Figure 2 shows the powder x-ray diffraction patterns for the SnO$_2$ doped MgB$_2$ sample and the control sample. It can be seen that in both samples MgB$_2$ is a major phase, and that some MgO was also formed during the sintering process. From the doped sample pattern, we do not see SnO$_2$, but we do see free Sn, indicating the expected decomposition of SnO$_2$ to Sn and oxygen. Further, the active Mg reacted with Sn to form the intermetallic compound Mg$_3$Sn.

Based on the XRD data, lattice parameters for these samples were extracted. The lattice parameters of the undoped sample are $a=3.086$ Å and $c=3.525$ Å, while those of the doped sample are: $a=3.085$ Å, and $c=3.524$ Å. There is no discernable lattice shift in $a$-axis and $c$-axis lattice parameters in MgB$_2$ phases for the doped sample, which is different from Dou’s work [3].

Our XRD results, while not speaking directly to oxygen doping per se, do allow us to look for MgB$_2$ lattice parameter shifts and the presence of gross second phases. Also, it allows us to look for presence of SnO$_2$ as well as free Sn – allowing us to see if SnO$_2$ has decomposed.

![XRD patterns for 5wt% SnO$_2$ doped MgB$_2$ and control MgB$_2$ samples.](image)

3.3. Magnetic response of the MgB$_2$ pellets

$B_{cr}$ and $B_{sc}$ as a function of temperature for the 5 wt% SnO$_2$ doped MgB$_2$ and the control MgB$_2$ bulk samples are shown in Figure 3. From the graph, we can see that in the temperature window between 24 K and 39 K, the doped sample has lower upper critical fields and irreversible fields than the control. In the 24-39 K window, there is approximately 0.5 T reduction in $B_{cr}$ and $B_{sc}$ for the doped sample as compared to the undoped sample. This result is different from Dou’s result [6], where Sb$_2$O$_3$ additions increased the $B_{cr}$ from 4.1 T (undoped sample) to 5 T at 29.2 K. Thus, under our specific preparation conditions we observed a decrease in the critical fields (within the temperature window we explored), rather than an increase with SnO$_2$ doping. This work only explored one doping level and one reaction heat treatment (HT), so we may not have found the optimum conditions. Also, we used an ex-situ route, rather than an in-situ one, and this may be an important factor.
4. Conclusion

An MgB$_2$ bulk sample has been fabricated with 5 wt% SnO$_2$ doping using an ex-situ processing route, and it has been compared to a control sample. SEM performed on the samples after powderizing shows similar grain structure in the doped and control sample. XRD measurements on the doped sample show no SnO$_2$, but the presence of free Sn, indicating the decomposition of SnO$_2$ during the reaction HT. XRD measurements show little or no change in c-axis lattice parameter, suggesting a lack of significant incorporation of oxygen into the lattice. A slight decrease in $B_{c2}$ and $B_{irr}$ was observed in the 24 K-39 K range. Addition of SnO$_2$ has slightly decreased $B_{c2}$ and $B_{irr}$ of MgB$_2$ given our particular preparation conditions of an ex-situ route and a 900°C reaction heat treatment. The mechanism is unclear, and may be connected either to the oxygen or the Sn from the decomposed SnO$_2$. We have only explored one reaction temperature and one reaction type (ex-situ), which leaves a large amount of parameter space to explore. Given the promising results seen with previous in-situ work [6], we think oxygen additions are worth further exploration.

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Figure 3 Temperature dependence of $B_{c2}$ and $B_{irr}$ of pure MgB$_2$ sample and SnO$_2$ doped sample.
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