Titania Doping Effect on Superconducting Properties of MgB$_2$ Bulk Samples

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Abstract. In this work we study the microstructural and superconducting properties of doped and undoped bulk MgB$_2$ samples prepared by solid-state reaction, with 0 and 2.5 %at. nominal TiO$_2$ nanotubes contents, annealed at different temperatures in the 750-900°C range. We discuss the $T_c$, $J_c$ and $H_{c2}$ performance and their correlation with the different synthesis parameters.

Index Terms — MgB$_2$, Titania Nanotubes doping, material synthesis effects.

1. Introduction
Since the discovery of superconductivity of MgB$_2$ countless studies have been conducted with the aim of improving their properties for potential technological applications. [1]-[5] Many groups have worked to improve the critical current density by the creation of defects through dopantes or additions that may serve as vortex-pinning centers, such as SiC, [6][9] CNT [10][14] and nano-TiO$_2$ [15]. These additions also improve the critical field through the chemistry substitution at the boron sites. At the same time, Gurevich et al. proposed that this chemical substitution affect the electron scattering between $\sigma$ and $\pi$ bands, and the diffusivity into the bands. These variations have a strong correlation with temperature dependence and values of critical fields.[17]-[19]

In this work we studied the influence of titania oxide (TiO$_2$) nanotubes (NT) incorporation into MgB$_2$ bulk samples over the microstructural ($a$-lattice parameter, MgO amount) and superconducting properties (critical current density, critical fields and critical temperature), and the influence of synthesis parameters.

2. Experiment Details

2.1. Sample preparation
The samples were prepared by solid-state reaction using as starting materials magnesium powder (-325 mesh, 99.8% Assay), amorphous boron powder (-325 mesh, 99.99% Alfa Aesar) and titania oxide nanotubes (outer and inner diameter ~10nm and 5-7nm respectively).[20] The powders were mixed...
using ball milling inside a N$_2$ atmosphere globe box, during 1 hour. The undoped sample was prepared only with Mg and B with 1.2:2 ratio and sintered at 900°C during 30 min and then naturally cooled down until room temperature. On the other hand, doped samples were made with addition of 2.5% at TiO$_2$NT, and sintered at temperatures of 750, 850 and 900°C during 150, 80 and 30 min respectively, the table 1 shows these synthesis parameters.

2.2. Microstructural characterization
X-ray diffraction patterns were taken in a Phillips PW 1700 with radiation Cu K$_α$ (1.5417 Å). The powders were mixed with Si standard in order to correct the peaks position of MgB$_2$ and MgO phases. The amount of MgO phase was calculated making a semi-quantitative analysis between MgB$_2$ and MgO amounts. The $a$-lattice parameter was determined taking into account the shifts in all the peaks.

2.3. Superconducting characterization
D.c. magnetization, $M$, of ~ 6 x 0.2 x 0.3 mm$^3$ long pieces of the samples, has been measured with the applied magnetic field H parallel to the long axis of parallelepiped, using a Quantum Design SQUID magnetometer up to 5T. We determined $T_c$ from $M$ vs $T$ curves with the onset transition criteria. $J_c$ was calculated from magnetization loops, $M(H)$, using the Bean model assuming uniform current density.

Resistivity measurements up to 12T using the four probe method was used to determine the upper critical field ($H_{c2}$) and irreversibility field ($H_{irr}$) for all samples listed in table 1. The residual resistance ratio ($RRR$) was determined as the ratio $\rho(290)/\rho(40)$. The $T_c$ from resistivity measurements was determined using the 50% transition criteria and the bar error as the difference between 10 and 90% of the transition.

Table 1. Characteristics of MgB$_2$ undoped and TiO$_2$NT doped samples

| Sample  | Composition: MgB$_2$ +… | Sintering Temperature | Sintering Time |
|---------|--------------------------|-----------------------|----------------|
| NT00-900| undoped                  | 900°C                 | 30 min.        |
| NT25-900| 2.5%TiO$_2$NT            | 900°C                 | 30 min.        |
| NT25-850| 2.5%TiO$_2$NT            | 850°C                 | 80 min.        |
| NT25-750| 2.5%TiO$_2$NT            | 750°C                 | 150 min.       |

3. Results and discussion

Figure 1. Normalized x-ray diffraction pattern for all samples listed in Table 1. The symbol * indicate the Si peaks used as internal standard.
3.1. X-rays analysis

The x-rays diffraction patterns for all samples listed in Table 1 are shown in Figure 1. All samples have MgO phase, observed as a peak at 2θ ~ 42°. The a-lattice parameters were calculated from the shifts of MgB$_2$ peaks and these are shown in Figure 2a. NT25-900 sample sintered at 900°C displays lower a-lattice parameter than NT-900. Doped samples sintered at lower temperatures exhibit higher a-lattice parameters than NT25-900; this may indicate that part of oxygen from titania nanotubes is introduced in the MgB$_2$ structure. Figure 2b displays the amount of MgO phase calculated from semi-quantitative analysis that compare the intensity and positions of the patterns. It can be observed that doped samples have more MgO content than NT00-900 due to the presence of TiO$_2$NT as oxygen source, furthermore, the MgO amount increases at lower sintering temperature.

![Figure 2. a) Lattice parameter a (calculated from peaks shifts), and b) MgO amount (estimated from semi-quantitative analysis) as a function of sintering temperature for samples listed in table 1.](image)

3.2. Magnetization measurements

Figure 3 shows the $J_c$ field dependence up to 5T for all samples investigated, calculated from magnetization loops at 5, 20 and 26.5K. At 5K samples NT00-900 and NT25-850 have the same $J_c$ values and higher than the others samples, but at 20 and 26.5K all doped samples have lower $J_c$ values than sample NT00-900. This result can be explained taking into account that doped samples have more amount of MgO, and hence the grains connectivity is reduced, this effect is of first order in comparison to vortex-pinning defects such as nanotubes. Figure 3 also shows the Kishan et al. [15] data for undoped and 2% nano-TiO$_2$, at 5 and 20K, in order to compare with our samples. Their undoped and doped samples have lower $J_c$ values than our NT00-900 sample, indicating that sintering parameters are more important than the kind of addition.

| Sample     | a-lattice parameter [Å] | MgO amount [%] | $T_c^{MF}$ [K] | $T_c^{Trans}$ [K] | RRR | Active area fraction, $A_f$ |
|------------|-------------------------|----------------|---------------|------------------|-----|-----------------------------|
| NT00-900   | 3.0854 ± 0.0003         | 7.0            | 38.2 ± 0.1    | 38.62 ± 0.08     | 2.66| 0.26                        |
| NT25-900   | 3.0843 ± 0.0004         | 10.4           | 38.4 ± 0.1    | 38.82 ± 0.08     | 2.82| 0.25                        |
| NT25-850   | 3.0846 ± 0.0003         | 11.0           | 38.3 ± 0.1    | 38.67 ± 0.08     | 2.54| 0.25                        |
| NT25-750   | 3.0858 ± 0.0004         | 13.8           | 38.1 ± 0.1    | 38.51 ± 0.08     | 2.41| 0.13                        |
The $T_c$’s obtained by magnetization are shown in Table 2. $T_c$’s decreases with higher $a$-lattice parameters. All width transitions are similar and lower than 0.4K, indicating that all samples are very homogeneous.

![Figure 3. Critical current density obtained by magnetization as a function of applied field for all samples listed in table 1. The lines are only a guide to eye.](image)

![Figure 4. Temperature dependence of $H_{c2}$ and $H_{irr}$ obtained from resistivity measurements until 12T for all samples investigated. The lines are only a guide to eye.](image)

3.3. $H_{c2}$ and $T_c$ obtained by transport measurements

Figure 4 shows the $H_{c2}$ and $H_{irr}$ as function of temperature, for all samples listed in table 1. We observed that doped samples sintered at higher temperatures have a small improvement in the $H_{c2}$ and $H_{irr}$ values; in contrast sample NT25-750 has an important $H_{c2}$ enhancement of 1T at 20K.

The $RRR$ and $T_c$ obtained by transport measurements are shown in Table 2, both are correlated with $a$-lattice parameter, and increase with doping level but decrease at low sintering temperature. This is caused by a shift to dirty limit.

The active area fraction $A_f$ was calculated according to the formula proposed by Rowell et al. [21] (see Table 2). These values estimate the degree of grain connectivity. We observed that $A_f$ increases with the sintering temperature, indicating that samples with higher sintering temperature have a better grain connectivity.

4. Summary

A study on the effect of 2.5%TiO$_2$NT doping and sintering temperatures in the 750-900°C range is presented.

Variations in the $a$-lattice parameter with doping and sintering temperature were observed. At $T_s$=900°C, the doped sample has a lower $a$-lattice parameter but when the $T_s$ decreases the $a$-lattice parameter increase, probably as a consequence of oxygen substitution into boron sites. The semi-quantitative analysis showed that all doped samples have more MgO amount, due to titania nanotubes addition work like an oxygen source.

The $J_c(H)$ of undoped sample is higher than the values of all doped samples for all the studied temperatures. This is correlated with the MgO amount present in the samples, which strongly suggest that the MgO amount is the main responsibly of $J_c$ behavior compared with any kind of vortex-pinning defects.
A strong correlation between $H_{c2}$ and $H_{irr}$ with $a$-lattice parameter was observed. This is in agreement with a theoretical model of Gurevich, in which any kind of substitution produces variation in the temperature dependence of $H_{c2}$.[17] An $H_{c2}$ improvement of 1T at 20K was measured for NT25-750 sample.

The titania nanotubes additions does not show a correlated enhancement between $H_{c2}$ and $J_c$ in contrast with carbon nanotubes addition, when both $H_{c2}$ and $J_c$ improve with additions.

Both $T_{c,trans}$ and $RRR$ present a good correlation with $a$-lattice parameter, indicating that the oxygen plays an important role in the transport mechanism, and that doped samples tend to the dirty limit.

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