Materials Chemistry and Physics 146 (2014) 313–323

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Addition of Ho_2O_3 of different types to MgB_2 in the *ex-situ* Spark Plasma Sintering: Simultaneous control of the critical current density at low and high magnetic fields

G. Aldica [a], S. Popa [a], M. Enculescu [a], D. Batalu [b], L. Miu [a], M. Ferbinteanu [c], P. Badica [a,*]

[a] National Institute of Materials Physics, Str. Atomistilor 105 bis, 077125 Magurele, Romania
[b] University 'Politehnica' of Bucharest, Splaiul Independentei 313, 060042, Romania
[c] University Bucharest, Inorg. Chem. Dept., Dumbrava Rosie 23, 020462, Romania

HIGHLIGHTS

- Two types of Ho_2O_3 powders (A and B) with different morphology were added to MgB_2.
- Samples were obtained by *ex-situ* Spark Plasma Sintering.
- Addition type influences vortex pinning and controls J_c at low or high fields (H).
- Addition of (A + B) enhances J_c at high H and minimizes its suppression at low H.

ARTICLE INFO

Article history:
Received 25 October 2013
Received in revised form
18 February 2014
Accepted 19 March 2014

Keywords:
Superconductors
Sintering
Microstructure
Superconductivity

ABSTRACT

Two different types of Ho_2O_3 powders (showing a much different morphology) were added to MgB_2 in the *ex-situ* Spark Plasma Sintering (SPS). In the 5–25 K range, the first Ho_2O_3 powder type does not significantly suppress the critical current density J_c at low magnetic fields and the second one enhances it at high fields, while their mixture simultaneously controls J_c at both small and high magnetic fields so that the decrease is small at low fields and there is a notable enhancement at high fields when compared to pristine sample. The control of $J_c(H)$ is discussed versus specific characteristics of the raw powders, the resulting microstructure of the added SPS-ed samples and pinning details from magnetic relaxation measurements.

1. Introduction

MgB_2 is a superconducting material [1] of high potential for different applications. It is a light, cheap and available material with a relatively high critical temperature (T_c) of ~39 K. Through doping, functional characteristics of MgB_2, such as the critical current density, J_c, may significantly increase [2,3] and become competitive when compared to other technical superconductors.

The previous works on MgB_2 doped with holmium or Ho-compounds used the *in-situ* technique that consist of:

(1) mixing pristine powders of Mg, B and the Ho-based dopant,
(2) cold pressing into pellets, and
(3) reaction leading to synthesis of MgB_2.

This approach usually needs special conditions such as encapsulation in Ta crucibles or other metal foils/tubes, and heating under inert or reducing atmosphere of Ar or Ar + H_2, respectively [4–8]. Although Ho-based doping leads to enhancement of J_c, samples produced by *in-situ* method usually show low densities, below 80–90%. Situation is similar for other rare earth based additions, such as rare earth oxides [8–14].

For achieving a high density, one can use the unconventional method of Spark Plasma Sintering (SPS) [e.g. [15,16]]. During SPS processing, on the punches of a graphite mold system loaded with the powder mixture to be sintered, a uniaxial pressure and a pulsed electrical field are applied. The consequences are high heating rates and occurrence of debatable unconventional activation processes [17]. The resulting material has usually high density, above 90%, and is composed of nano grains. A nanostructured MgB_2 is convenient because more grain boundaries are introduced in the material. Grain boundaries [18] are well known to be efficient pinning sites in MgB_2 enhancing J_c.

* Corresponding author. Tel.: +40 21 3690170; fax: +40 21 3690177.
E-mail address: badica2003@yahoo.com (P. Badica).

http://dx.doi.org/10.1016/j.matchemphys.2014.03.030
0254-0584/

Table 1
Samples, starting composition, apparent density (ρa^{SPS}), relative density (R^{SPS}), lattice constants, average XRD crystallite size and wt.% of the secondary phases (W) for all samples.

Sample	Composition	ρa^{SPS} [g cm^{-3}]/R^{SPS} [%]	Lattice constants		Average XRD crystallite size [nm]				W [wt. %]		
			a [Å]	c [Å]	MgB_2	MgO	HoB_4	MgB_4	MgO	HoB_4	MgB_4
Powder	Powder MgB_2	–/–	3.0878	3.5249	250 ± 100	–	–	–	~1.0	–	–
SPS-P	MgB_2	2.52/93.8	3.0832	3.5244	252^{+167}_{-72}	125 ± 140	–	100 ± 14	7.3	–	7.9
SPS-A	$(MgB_2)_{0.975}$(A-$Ho_2O_3)_{0.0125}$	2.63/93.4	3.0830	3.5255	180^{+200}_{-50}	30^{+2}_{-1}	45 ± 4	(350^{+250}_{-100} for $HoO_{1.5}$)	11.0	5.0 (incl. 1.0 of $HoO_{1.5}$)	12.4
SPS-B	$(MgB_2)_{0.975}$(B-$Ho_2O_3)_{0.0125}$	2.70/98.1	3.0833	3.5295	115^{+30}_{-15}	57 ± 6	45^{+7}_{-4}	50 ± 2	8.5	4.8	11.5
SPS-(A + B)	$(MgB_2)_{0.975}$(A-$Ho_2O_3)_{0.00625}$(B-$Ho_2O_3)_{0.00625}$	2.74/99.5	3.0831	3.5302	175^{+100}_{-20}	31 ± 4	56 ± 1	140^{+50}_{-20}	8.2	4.8	12.0

In this work MgB_2 samples doped with Ho_2O_3 were prepared by *ex-situ* SPS. In the *ex-situ* routes powder of MgB_2 is used instead of the mixture of Mg and B as for the *in-situ* approaches. We observe J_c enhancement as for the *in-situ* approach when Ho_2O_3 addition is used. However, enhancement strongly depends on the type of the raw Ho_2O_3 addition powder. Remarkable is that by adding Ho_2O_3 of different type it is possible to control the shape of $J_c(H)$ curve towards simultaneous maximization of this parameter at low and at high fields in the 5–25 K range.

2. Experimental

The commercial MgB_2 powder was supplied by Alpha Aesar (99.5% purity). The Ho_2O_3 powder of type A was from Johnson-Matthey, Fluka & Co Ltd. (99.9% purity) and Ho_2O_3 of type B from Aldrich (99.9% purity). The MgB_2 and Ho_2O_3 raw powders were mixed for 15 min in an agate mortar. Starting composition of the samples was constant $(MgB_2)_{0.975}(Ho_2O_3)_{0.0125}$. This stoichiometry was selected based on literature data for maximum J_c [4,7] when Ho_2O_3 nano powder was added to MgB_2 in the *in-situ* conventional processing. The MgB_2 pristine powder or the powder mixtures (3 g) of MgB_2 with Ho_2O_3 of different types (Table 1) were wrapped into carbon paper, loaded into a 2.08 cm diameter graphite die and processed by Spark Plasma Sintering (SPS) at 1150 °C for 3 min. Heating rate was 110°C min^{-1} and the maximum pressure applied on samples was 95 MPa. The sintering process was made in a FCT Systeme GmbH – HP D 5 (Germany) spark plasma sintering system. The initial vacuum in the SPS furnace was 40 Pa. The temperature was measured using a pyrometer at 2 mm above the sample, on the punch surface and through an axial hole. A pulsed current pattern of 12-on/2-off pulses was applied, with a 3 ms period. The total time of one sequence was ~0.04 s. The operating voltage and the peak current were up to 5 V and 1600 A. More details on SPS of MgB_2 are presented in Ref. [19].

X-ray diffraction (XRD) patterns (at $T = 25$ °C) were measured by a Bruker AXS D8 Advance diffractometer ($CuK_{\alpha 1}$ radiation, $\lambda = 1.5406$ Å). Rietveld analysis was performed (MAUD software [20] version 2.31) and lattice constants, weight fraction of phases (W) and crystallite sizes of each phase were extracted using Williamson-Hall method (Table 1).

The Fourier transformed infrared (FT-IR) spectra on our powders mixed with reference substance KBr were measured on a Jasco 4200 FT-IR spectrometer.

Apparent densities ρa^{SPS} (g cm^{-3}) of the sintered pellets were determined by Archimedes method using a KERN ALT 220-4M density balance (Table 1). Theoretical density ρt^{SPS} (g cm^{-3}) of the composite was determined according to ref. [21] considering that samples according to XRD contain MgB_2 (2.63 g cm^{-3}), MgO (3.58 g cm^{-3}), HoB_4 (6.896 g cm^{-3}) [22], Ho_2O_3 (8.405 g cm^{-3}) [23] and MgB_4 (2.49 g cm^{-3}). The relative density of the SPS-ed samples, R^{SPS} (%) is the ratio $\rho a^{SPS}/\rho t^{SPS} \times 100$. Curves of relative density evolution during SPS were plotted based on punches displacement, d (mm) following the procedure described in ref. [19]. Displacement was measured *in-situ* by SPS machine vs. time, t (sec.).

Scanning electron microscopy (SEM) images were taken with Zeiss EVO50. For bulks, observations were made on fresh surfaces obtained by fracturing the samples. Transmission electron microscopy (TEM) measurements were performed using a Tecnai G2 F30 S-TWIN/2006 microscope.

The magnetic measurements were carried out on samples having dimensions of ~1.5 × 1.5 × 1 mm^3, cut from the center of the sintered disc using an oil cooled saw. A VSM magnetometer (Cryogenic, 9 T) was used. The magnetic field H was applied in zero-field cooling (ZFC) conditions and oriented perpendicular to the largest sample side. The field rate was 100 Oe s^{-1}. After the correction of the magnetic hysteresis curves due to magnetic contribution of the nonsuperconducting inclusions, of the sample holder and the sample reversible magnetization, the critical current

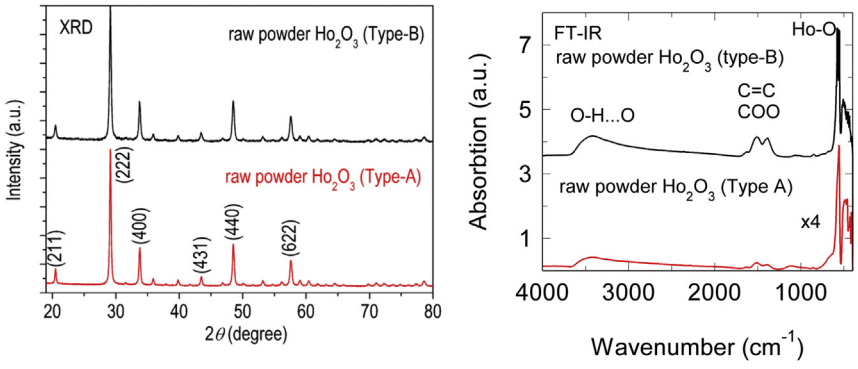

Fig. 1. XRD and FT-IR patterns for Ho_2O_3 raw powders of type A and B added to MgB_2 superconductor.