Available online at www.sciencedirect.com

SciVerse ScienceDirect

Journal of the European Ceramic Society 34 (2014) 337–346

www.elsevier.com/locate/jeurceramsoc

Control of barium ferrite decomposition during spark plasma sintering: Towards nanostructured samples with anisotropic magnetic properties

Simona Ovtar [a], Sophie Le Gallet [b,*], Ludivine Minier [b], Nadine Millot [b], Darja Lisjak [a]

[a] *Department for Material Synthesis, Jozef Stefan Institute, Ljubljana, Slovenia*

[b] *Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 6303 CNRS – Université de Bourgogne, BP 47870, Dijon Cedex, France*

Received 23 May 2013; received in revised form 19 July 2013; accepted 29 July 2013

Available online 4 September 2013

Abstract

The sintering of barium ferrite (BaM) nano-sized powders by spark plasma sintering was studied. At the surface of the samples, an iron-rich layer (magnetite) was formed due to the decomposition of BaM and segregation in the secondary phases. To prevent the formation of secondary phases different protection layers between the graphite mould and the sample were used. Their effect on the sample microstructure was studied by X-ray diffraction and scanning electron microscopy. The most suitable protection layer was a highly dense sintered disc of aluminium oxide. Using this dense protection layer, sintered discs of BaM with 82% of theoretical density and grains of 90 ± 50 nm were obtained. A magnetic anisotropy was achieved from the sintering of the BaM particles with the largest shape anisotropy.

Keywords: Ferrite; Magnetic properties; Spark plasma sintering; Decomposition; Protection layers

1. Introduction

Barium ferrite ($BaFe_{12}O_{19}$, BaM) is a hard-magnetic material, with a high coercive field and a high remanent magnetization. The crystal structure of BaM is the magnetoplumbite type (M-type) which is the simplest crystal structure of hexaferrites.[1] The unit cell is composed of the S-block and the R-block with cubic-close-packed and hexagonal-close-packed oxygen ions, respectively. In the S-block, tetrahedral and octahedral sites are partially occupied by the iron ions and the crystal structure is spinel-like, like magnetite and maghemite.[1] In the R-block, the iron ions occupy three different sites and the barium ions (the largest ions) form together with the oxygen ions the hexagonal-close-packed structure.[1] The BaM unit cell is anisotropic and elongated along the *c* axis. The magnetic properties of BaM originate from the ordering of the iron ions magnetic moments in the crystal structure. The preferential axis of the magnetic moments coincides with the crystallographic axis *c*, leading to magnetic moments aligned perpendicularly to the basal-plane of the plate-like particles. Such a magneto-crystalline anisotropy results in hard magnetic properties, explaining that BaM is used as permanent magnet. The other applications of BaM are for millimetre-wave devices, like absorbers and non-reciprocal devices, due to the high ferromagnetic resonance frequency, which also is a consequence of high magneto-crystalline anisotropy field. For most of applications, dense materials with small grain size are required. The preparation of bulk materials by conventional nanopowder sintering mostly leads to materials with low density.[2] In addition, sintering of BaM is accompanied with an abnormal and exaggerated grain growth.[3] In BaM grains of sizes above 1 μm, a multi-domain structure is formed and the magnetic properties are changed.[4] Specially, the coercivity and remanent magnetization are decreased. Therefore, to preserve a single-domain structure and to produce dense material, non-conventional sintering techniques must be used, like spark plasma sintering (SPS). SPS allows increasing the density of sample with minimal grain growth and consequently is a suitable sintering method for the preparation of dense nano-ceramics.

BaM bulk materials with high remanent magnetization and high coercive field have already been prepared by SPS. Either BaM powder[5] or precursors of BaM prepared by precipitation of barium and iron ions[6–9] were sintered. Concerning the latter case, synthesis and sintering of BaM occur in a single SPS

* Corresponding author. Tel.: +33 3 80 39 61 63; fax: +33 3 80 39 61 67.
E-mail address: sophie.le-gallet@u-bourgogne.fr (S. Le Gallet).

0955-2219/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jeurceramsoc.2013.07.027

experiment. The sintering of BaM by SPS mostly leads to formation of a non-stoichiometric BaM with secondary phases[6] like nano-belts and nano-rods with atomic Fe/Ba ratio in the range 7–18 and barium-rich phase with atomic Fe/Ba ratio of 3.[9] The secondary phases in SPS sintered bulks are mostly formed due to the reductive atmosphere. Reduction of oxide materials during sintering were observed for many materials.[10–14] For Mn–Co oxide spinels, Bordeneuve et al.[10] reported that the secondary phases ($(Mn_{1-x/3}Co_{x/3})O$) were formed at the surface of the sintered sample. Yamamoto et al.[12] measured the magnetic properties of a sliced Mn–Zn ferrite; the poorest properties were obtained for the slice corresponding to the surface. The thickness of secondary phase layer is mostly a few dozen of μm and can be easily removed from the bulk samples by grinding. The problem appears in sintering of films with thickness of a few dozen of μm. For these samples, decomposition would be total. To prevent decomposition, Kim et al.[15] added bulk ZrO_2 cylinders between the graphite punches and the sample (a thick film of $YBa_2Cu_3O_x$ prepared by screen printing). Santanach et al.,[11] in turn, inserted an alumina powder bed. Due to reduction, most of authors use the post-sintering heat treatment to re-oxidize and improve the specific properties of materials.[14,16–19] However, it is also reported that the re-oxidation of the sample core is difficult due to the high density and closed porosity of sintered materials.[19]

In this study we show that by using an adapted protection layer between the sample and the graphite mould, the formation of secondary phases can be prevented and magnetic properties of BaM specimens measured.

2. Experimental procedure

A commercial BaM powder (99.5% purity, Aldrich, noted C) and a home-prepared one synthesized by a hydrothermal method (noted H) were used. The powder H was synthesized at 240 °C (with a heating rate of 3 °C/min, without holding time), from iron and barium nitrates in the 5:1 molar ratio. Sodium hydroxide was used as precipitant agent. Hydroxides were precipitated. Addition of dodecylbenzenesulphonic acid (DBSa) was added and suspension was decanted into an autoclave (model 4522M, Parr Instrument Co.). After synthesis the powder was washed with water, nitric acid and acetone. The remaining organic compounds were removed using a heat treatment at 460 °C for 2 h with a heating rate of 0.5 °C/min. Synthesis is described in details elsewhere.[20] The particle diameter and thickness were determined from TEM (JEOL 2100) images, by averaging the dimensions of more than 500 particles. The powder H (after removal of the organics) is composed from plate-like particles of diameter from 10 to 500 nm (with a large proportion of particles around 10–60 nm in diameter) and thickness from 3 to 18 nm. The atomic Fe/Ba ratio, measured by chemical analysis (ICP-AES, PE OPTIMA 3100RL), is 12.5 ± 1.0. The powder C has particles of diameter from 10 to 130 nm and thickness from 6 to 90 nm. The atomic Fe/Ba ratio is 13.0 ± 0.7. The magnetic properties of the powders were measured at the magnetic field of 10 kOe with a vibrating-sample magnetometer (VSM, HLake Shore Cryotronics, Inc.H). At 10 kOe, the powder C has hard-magnetic properties with a magnetization of 31 emu/g and a high coercivity of 3840 Oe at ambient temperature. Under the same conditions, the powder H has weaker magnetic properties with a magnetization of 28 emu/g and a coercivity of 1570 Oe at 10 kOe.

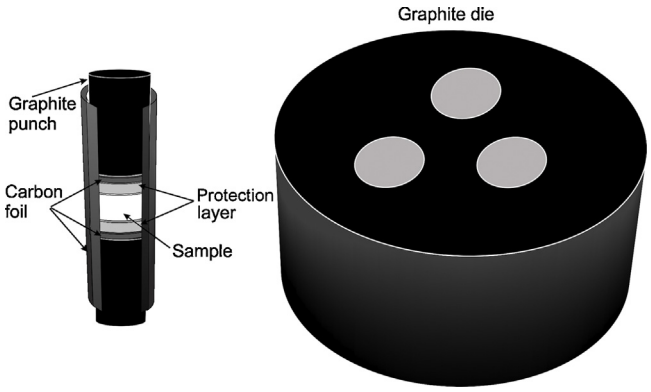

Fig. 1. Schematic presentation of the sample set-up in mould.

Powders C and H (1.3 g) were sintered in a graphite mould by SPS (FCT System GmbH, HPD125 apparatus). The graphite die is 40 mm high and 80 mm large and allows sintering of three samples (13.5 mm diameter, 2 mm thick) at the same time (Fig. 1). A carbon foil (Carbone Lorraine, 0.37 mm) surrounds the holes in order to ensure a better electrical contact between the die and the punches. The sticking of BaM to the graphite punches was prevented by intercalating also this carbon foil at the bottom and at the top of the BaM powder, as shown in Fig. 1. The BaM powders were sintered at 900 °C with a holding time of 30 min under vacuum. The heating rate was 50 °C/min and the uni-axial pressure applied during sintering was 50 MPa.

The different protection layers evaluated were carbon foil with sprayed BN (Advanced Ceramics corporation) (sample C-BN), carbon foil with sputtered gold (sample C-Au), alumina powder bed (Materion, 325 mesh) (samples C-pAl_2O_3 and H-pAl_2O_3) and alumina discs (with 96% of theoretical density) (samples C-bAl_2O_3 and H-bAl_2O_3). The protection layer was in direct contact with the BaM powder, as shown in Fig. 1. The thickness of alumina powder bed or disc was 1.6 mm. Sample sintered without protection layer is denoted C-C (due to carbon pollution coming from the carbon foil).

To compare the SPS samples with the conventionally sintered ones, powders C and H were also sintered at 1350 °C with a heating rate of 5 °C/min for 3 h under air atmosphere in a conventional furnace.

The densities of samples were measured with the Archimedes method in distilled water. The crystal structures of sintered samples were confirmed by X-ray diffraction (XRD, Cu*K*α radiation, Siemens Bruker, D8). The grain size was determined with a scanning electron microscope (SEM, JSM-7600F, JEOL) on polished cross sections, which were chemically etched by aqueous solution of HBr. The secondary phases were investigated with SEM backscattered electrons (BEI mode) on polished cross sections. The average thickness of secondary phase layers was measured at the top and bottom of the samples. The chemical composition of the sintered samples was explored with an