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A study of magneto-crystalline alignment in sintered barium hexaferrite fabricated by powder injection molding

B.S. Zlatkov [a], M.V. Nikolic [b,*], O. Aleksic [b], H. Danninger [c], E. Halwax [c]

[a] FOTEC Forschungs- und Technologietransfer GmbH, Viktor Kaplan-Strasse 2, 2700 Wiener Neustadt, Austria
[b] Institute for Multidisciplinary Research, Kneza Viseslava 1, 11000 Beograd, Serbia
[c] Institute of Chemical Technologies and Analytics, Getreidemarkt 9/164, 1060 Wien, Austria

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ABSTRACT

Barium hexaferrite permanent magnets were produced by powder injection molding. Starting barium hexaferrite powder was prepared from a Fe_2O_3 and $BaCO_3$ powder mixture by calcination followed by milling. The feedstock for powder injection molding was prepared by mixing barium hexaferrite powder with a low viscosity binder. Magnetic alignment was achieved by applying a high intensity magnetic field to the melted feedstock during the injection process. Green samples (with and without magnetic alignment) were subjected to solvent debinding and subsequent thermal debinding followed by sintering. Sintering conditions were optimized in order to achieve a maximum energy product value. Magneto-crystalline aligning in barium hexaferrite was studied on both green and sintered samples using X-ray diffraction, scanning electron microscope (SEM) and magnetic measurements (hysteresis-graphs). All measurements were made both in a parallel and perpendicular direction to the aligning magnetic field. The obtained results confirmed magneto-crystalline alignment.

1. Introduction

Barium hexaferrite ($BaFe_{12}O_{19}$) is a hexagonal (M-type magnetoplumbite, space group $P6_3/mmc$) ferrimagnetic ceramic material with an easy magnetization along the *c*-axis. It is widely applied due to its low production cost combined with excellent magnetic properties. It has a high Curie temperature, a high coercive force and magneto-crystalline anisotropy along the *c*-axis and is also chemically stable and corrosion resistant. This has enabled production of magnetic recording media, ferrofluids, sensors and microwave absorbing materials [1–8]. Barium and strontium hexaferrites have been applied as ceramic magnets in loudspeakers and rotors in small DC motors [1]. Today they are mass produced in many factories by wet pressing and sintering. Textured barium hexaferrite is commonly used in permanent magnets [2]. Much attention has been paid to the preparation method of $BaFe_{12}O_{19}$ powder as this plays an important role in determining magnetic and structural properties [4]. Particle characteristics, including homogeneity, morphology and magnetic properties are influenced by the synthesis method. Various methods have been used besides the classical method of calcination, such as sol–gel [3], sol–gel combustion [4], sol–gel including additional precursor milling [4], combustion [6], co-precipitation [7,9–11] and magnetic field assisted gel casting [2].

The powder injection molding (PIM) technology is widely used for the production of numerous components from metal or ceramic powders, including asymmetric and complex core shapes that cannot be achieved by wet pressing and sintering [12,13]. The feedstock is composed of the starting powder, in this case hexaferrite, and a binder based on wax, thermo-plastics and additives [14]. The procedure involves mixing of the starting powder with binders (feedstock preparation), injection molding (“green” sample formation), debinding (formation of “brown” parts) and sintering. The binder composition is crucial to the PIM technology. Compared to other technologies the amount of binder mixed with the starting powder can be up to 45 vol% enabling viscous flow and thus injection molding of the feedstock. The binder must be successfully removed without distortion and contamination of the compact prior to sintering [15,16]. Two stages of the debinding process are applied: the first is solvent debinding that is followed by thermal debinding of the residual binder, the “backbone” (by burning in air). Thermal debinding is performed in a debinding furnace (with air flow to remove gases). Sintering conditions are optimized in order to

* Corresponding author.
E-mail address: mariavesna@cms.bg.ac.yu (M.V. Nikolic).

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achieve, in the case of magnetic materials, a maximum energy product $(B \times H)_{max}$.

Texturing (imposing a preferred orientation or "texture" on a crystalline material) ceramic material can result in nearly single-crystal properties [2,17–19]. Magnetic alignment results in particles aligned along the easiest magnetization axis. Traditional methods start with anisotropic powders and align them using uniaxial pressing at high temperatures to rearrange grains or viscous shear forces. Templated grain growth uses shear force during green body forming to align large anisotropically shaped templates. More recently a combination of magnetic alignment and gel casting has been used to obtain textured $BaFe_{12}O_{19}$ [2] and $Bi_4Ti_3O_{12}$ [17]. Thus, strontium ferrite powder has been used for the fabrication of permanent magnets [15,16]. In Ref. [15] PIM was used in combination with magnetic alignment by applying a magnetic field during the injection process to produce Sr-ferrite permanent magnets with magnetic parameter values above the current requirements for industrial applications.

In this work we have prepared grain oriented $BaFe_{12}O_{19}$ ceramics by magnetic alignment during PIM. Optimal injection parameters and the sintering regime were determined in relation to structural and magnetic properties of green and sintered samples.

2. Experimental

Starting $BaFe_{12}O_{19}$ powder was prepared from a powder mixture of Fe_2O_3 (99.9%, Aldrich) and $BaCO_3$ (99%, Sigma-Aldrich) by calcination at 1000 °C for 2 h followed by milling in slow ball mills for 24 h.

The feedstock composition was prepared by mixing the $BaFe_{12}O_{19}$ powder with a binder called "Solvent System" containing mainly wax, thermo-plastics and additives. Binder content was about 14 wt%. A Battenfeld HM 600/130 hydraulic drive injection molding machine was fed with the feedstock and injection was performed. Different experiments were done with varying injection parameters to achieve maximum magnetic flux density (mold temperature, feedstock melted temperature, injection pressure, etc.) The main parameters of injection are given in Table 1. Particle alignment was realized using a custom designed tool with a solenoid for switching on an axial DC magnetic field of 800 kA/m (0.63 T). All investigated samples had a disc shape. Solvent debinding was first performed followed by thermal debinding at a low temperature in a furnace at the start of the sintering process.

Sample density was determined using a helium pycnometer. The microstructures of the starting powder, green and sintered samples were studied on a SEM FEI Quanta 200 Mk2 device. The average particle size of the starting powder was determined from the obtained SEM micrographs. Magnetic measurements were performed on a Walker MH-10 hysteresisgraph.

Table 1
Powder injection moulding (PIM) parameters

PIM parameter	
Injection temperature (°C)	140
Tool temperature (°C)	40
Back pressure (MPa)	5
Injection speed (cm^3/s)	10
Injection pressure (MPa)	80
Holding pressure (MPa)	65
Holding time (s)	5
Filling time (s)	2.1
Cooling time (s)	30

Sintering was performed in the temperature range 1180–1260 °C for 1 h. After selecting the optimal sintering temperature (1200 °C) in view of the resulting sample density and the magnetic properties, the sintering time was varied and the optimal sintering conditions were determined as 1200 °C and 2 h taking into account the results obtained for $(B \times H)_{max}$ using a hysteresisgraph (Fig. 1).

Samples were denoted in the following way (sketch given in Fig. 2):

- GIN, green sample, isotropic (no magnetic alignment), SIN—after sintering, the top sample surface was studied;
- GAN, green sample, anisotropic (with magnetic alignment), SAN—after sintering, the top sample surface was studied in the *c*-axis direction;
- GAQ, green sample, anisotropic (with magnetic alignment), SAQ—after sintering, side surface—obtained by cutting cross-sections of disc-shaped samples.

X-ray diffraction measurements were performed on a Panalytical X'Pert PRO system, 2θ range 5–100°, Cu K_α radiation, by using either a graphite monochromator and a step scan mode with steps of 0.02° and a measuring time of 2.5 s per step, or a X'Celerator detector with Ni K_β filter where the scan length was ca. 2.5° with 25 s measuring time per scan length. Structural refinement was carried out by the Rietveld method using the GSAS package [20] with the EXPGUI graphical user interface [21]. The crystal structure parameters for $BaFe_{12}O_{19}$ used in the Rietveld refinement are

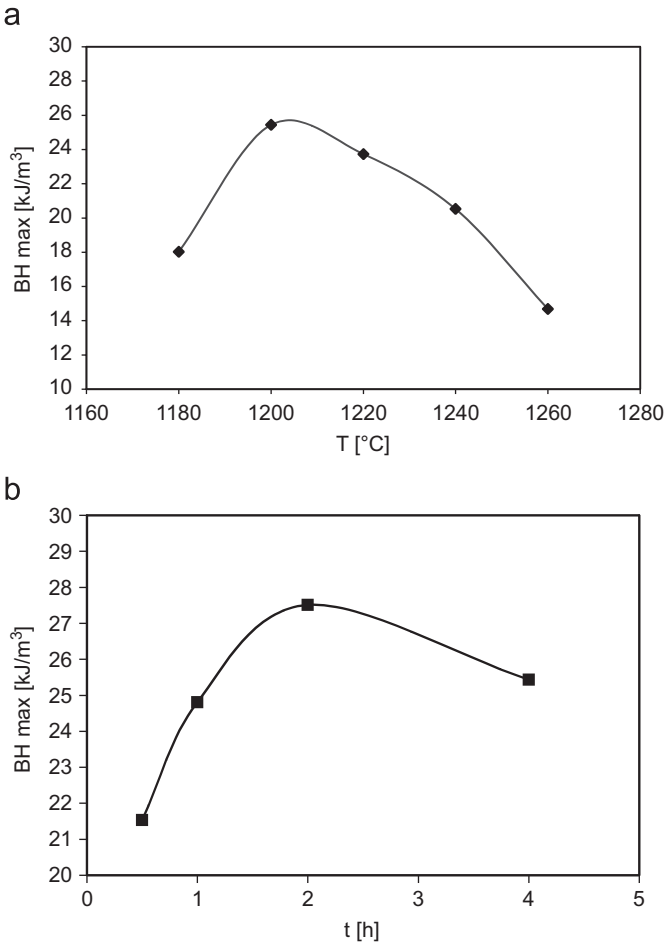

Fig. 1. $(B \times H)_{max}$ measured on the top surface of a sintered magnetically aligned $BaFe_{12}O_{19}$ sample: (a) different sintering temperatures, sintering time 1 h and (b) sintering temperature 1200 °C, different sintering times.