Materials Science and Engineering B 176 (2011) 8–13

Contents lists available at ScienceDirect

Materials Science and Engineering B

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

Barium hexaferrite nanoparticles: Synthesis and magnetic properties

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ARTICLE INFO

Article history:
Received 10 April 2010
Received in revised form 9 July 2010
Accepted 28 August 2010

Keywords:
Barium hexaferrite
Nanoparticles
Carbon combustion synthesis
Sintering
Magnets

ABSTRACT

Carbon combustion synthesis is applied to rapid and energy efficient fabrication of crystalline barium hexaferrite nanoparticles with the average particle size of 50–100 nm. In this method, the exothermic oxidation of carbon nanoparticles with an average size of 5 nm with a surface area of 80 m^2/g generates a self-propagating thermal wave with maximum temperatures of up to 1000 °C. The thermal front rapidly propagates through the mixture of solid reactants converting it to the hexagonal barium ferrite. Carbon is not incorporated in the product and is emitted from the reaction zone as a gaseous CO_2. The activation energy for carbon combustion synthesis of $BaFe_{12}O_{19}$ was estimated to be 98 kJ/mol. A complete conversion to hexagonal barium ferrite is obtained for carbon concentration exceeding 11 wt.%. The magnetic properties H_c~3000 Oe and M_s~50.3 emu/g of the compact sintered ferrites compare well with those produced by other synthesis methods.

1. Introduction

A barium ferrite with basic formula $BaFe_{12}O_{19}$, space group $P6_3/mmc$, has been widely used as a hard magnetic material for permanent magnets since its first introduction by Philips [1]. Their magnetic properties arise from interactions between metallic ions occupying particular positions relative to the oxygen ions in its hexagonal crystalline structure. Ba- ferrites have been used in various components for application at high frequency range due to their very low electrical conductivity, high magnetic anisotropy, high Curie temperature, mechanical hardness, excellent chemical stability and corrosion resistivity [2,3]. Recent studies have focused on the synthesis of nanocrystalline powders in order to improve magnetic properties with increasing the surface area of the nanopowders to enable sintering of pressed articles at a lower temperatures and fabrication of dense ceramics achieving theoretical density. There has recently been increasing interest in the use of barium ferrite also in the recording media applications with the emphasis on high-density perpendicular magnetic recording [4] where nanocrystaline magnetic thin-film media is required. Furthermore, the nanoscale magnetic ferrites are of particular interest due to their chemical compatibility with biological tissues and their unique combination of electronic and magnetic properties [5].

Barium hexaferrite particles can be produced by several processes, which differ in the production price and product properties. The oldest and most common one involves calcinations of a mixture of blended reactants (oxides or carbonates) in a furnace at temperature of up to 1200 °C for periods of 2–8 h [6,7]. This method requires use of high capital investment high temperature furnaces and high-energy consumption. Due to the long processing at high temperatures, the resultant particulate size of ferrite powders produced by calcination is large and requires further extensive processing to reduce grain size to enable desired magnetic properties. Several methods such as co-precipitation, glass crystallization, hydrothermal synthesis, sol-gel techniques, organo-metallic, microemulsion, spray deposition, organic ligand-assisted supercritical water process and other processes have been developed for preparing nanoparticles of barium ferrite [8–12]. However, all wet-chemical methods have several drawbacks: high pH sensitivity, stringent drying conditions, use of complex equipments and expensive precursors and disposal of the by-product. Also, most of the wet-chemical methods produce an amorphous structure that requires, in general, calcination at a high temperature to obtain a product with the desired magnetic properties and crystal structure. While the wet-chemical processes can produce high quality powders, the production costs are much higher than in calcination. The cost-effective preparation of mono-disperse particles of barium ferrite in the nano size (less than 100 nm) remains a challenge.

In this paper we present a novel method [13–15] to produce barium hexaferrite $BaFe_{12}O_{19}$ nanoparticles by Carbon Combustion Synthesis of Oxides (CCSO). In CCSO the exothermic oxidation

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doi:10.1016/j.mseb.2010.08.005

of carbon $C + O_2 = CO_2$ $\Delta H^{298}_{CO_2} = -393.5$ kJ/mol generates a steep thermal reaction wave (temperature gradient of up to 500 °C/cm) that propagates through a solid reactant mixture converting it to a desired complex oxide product. This method was successfully applied for simple, economical and energy efficient production of several complex oxides nanoparticles [13–18]. The motivation of this study was to test if CCSO method can produce Ba–ferrite nanoparticles with hard magnetic properties.

2. Experimental

Barium hexaferrite nanoparticles were produced by CCSO via the following reaction:

$$BaCO_3 + 6Fe_2O_3 + \alpha(C + O_2) = BaFe_{12}O_{19} + (\alpha + 1)CO_2 \qquad (1)$$

The reactants mixture used in CCSO contained up to 30 wt.% carbon nanoparticles “carbon acetylene” with the average particle size of 5 nm (surface area ~80 m^2/g) and non-combustible iron oxide and barium carbonate reactants with particle size ~50 nm. The molar ratio among the reactants was set according to the stoichiometry of $BaFe_{12}O_{19}$. The reactants were dried at 115 °C for 5 h before mixture preparation. Then the reactants thoroughly mixed together by using high-energy milling for about 2 h. The combustion synthesis was conducted by loading a loose mixture into a ceramic boat that was placed inside a cylindrical stainless steel vessel (ID = 70-mm and 60-mm length) fed by oxygen (purity 99.9+) at a flow rate at 10 l/min.

To initiate the propagating temperature front the reactant mixture was locally ignited by an electrically heated coil. The local combustion temperature (T_c) was measured by inserting in the center of the sample an *S*-type (Pt–Rh) thermocouple of about 0.1 mm diameter. The thermocouple readings were recorded and processed by an Omega data acquisition board connected to a PC.

The effluent gas composition was measured by a mass spectrometer Pfeiffer- D35614 OmniStar. The carbon content of the as-synthesized product was determined by a carbon analyzer (Leco, WR-112). The composition and crystal structure of the products was analyzed by X-ray diffraction (Siemens D5000 diffractometer) with Cu K_α radiation (λ = 1.54056 Å). Particle morphological features and microprobe analysis were determined by transmission (TEM, JEOL JEM-2000 CX2) and scanning electron microscopy (SEM; JEOL JAX8600, Japan) of loose powder fixed to a graphite disk. Particle size distribution and the particles surface area were determined by a Coulter SA 3100 BET analyzer.

The magnetic properties of the samples were measured at room temperature using a vibrating sample magnetometer VSM (Lake Shore Cryotronics, Inc. Model 7300) with an applied field up to 10^4 Oe.

3. Results and discussion

3.1. Thermal front propagation and synthesis of hexaferrite

The impact of the carbon concentration on the maximum reaction temperature during the CCSO of barium ferrite is shown in Fig. 1. The maximum reaction temperature increases with increasing carbon concentration in the reactant mixture. The combustion proceeded in an unstable mode and the front extinguished after moving for ~5 mm for mixtures containing ~5 wt.% of carbon nanoparticles. A reaction with a stable propagating temperature front was attained for reactant mixtures containing more than 6.5 wt.% of carbon. The stable front motion generated using 8–30 wt.% of carbon led to maximum temperatures of 900–1200 °C, well below the melting temperature of the $BaFe_{12}O_{19}$ product (~1600 °C) and of the carbon (3550 °C). Decreasing the heat generation and increasing the heat loss at the combustion zone may destabilize the reaction leading to a non-constant velocity of the reaction front or even extinction of the reaction front propagation. As expected, the average particle size (see SEM images in Fig. 1) increased with increasing combustion temperature and particles shape became irregular as the carbon concentration was increased. The maximum temperature approached an asymptotic value of about 1200 °C at a carbon concentration of 30 wt.%.

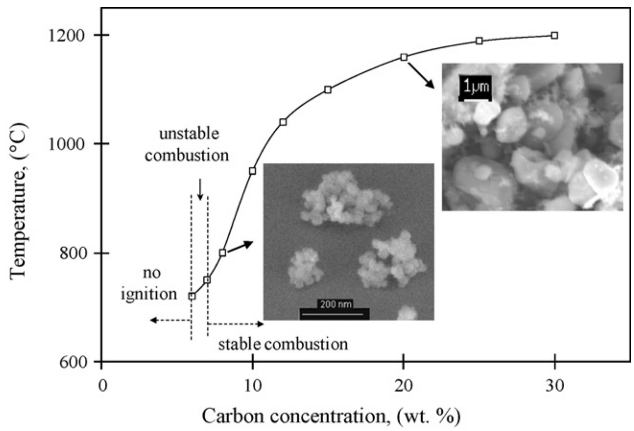

Fig. 1. The influence of the carbon concentration in the mixture on the maximum reaction temperature during the carbon combustion synthesis of $BaFe_{12}O_{19}$ via reaction (1). Insert: SEM images of $BaFe_{12}O_{19}$ particles.

Typical temporal temperatures at the center of the sample for the combustion reactions at 8, 10 and 12 wt.% are shown in Fig. 2. The temperature in the reaction zone increased at a rate of 40–60 °C/s and the total reaction time was about 180 s. The temperature profile at the 8 wt.% carbon clearly shows in curve a temperature drop indicating the endothermic effect at 750 °C that probably corresponds to the barium carbonate decomposition by $BaCO_3 \rightarrow BaO + CO_2$. At the carbon concentrations more than 10 wt.% the temperature drop at 750 °C is not possibly due to high exothermisity of the reaction. The reaction front propagated at a relatively slow velocity of about 1.3 mm/s using reactants mixture with 12 wt.% carbon and formed a friable and porous product. The stability of the thermal front propagation affects the quality of the CCSO products. The planar thermal front propagation is needed to produce a homogeneous product. These experiments revealed that reaction time of barium ferrite formation by CCSO is significantly fast (about minutes) than the common calcination method (usually hours).

3.2. Influence of oxygen flow rate

The oxygen flow rate is an additional tool in the CCSO process for controlling the reaction temperature, reaction time and subsequent Ba–ferrite structure. Oxygen flow rate also affects to the stability of the front propagation, because its transports the oxidizer and corresponding heat to the reaction zone. The maximum reaction temperature increased as the oxygen flow rate to the reactor was increased (Fig. 3). When process is conducted under low oxygen flow rates the reaction temperature and front velocity is low because of the oxygen limitations to the reaction zone. Increasing the flow rate from 2.2 l/min to 12 l/min increases the maximum temperature by about 200 °C, which affects to develop large particle size of the Ba–ferrite. Consequently, for complete conversion of the carbon to CO_2 during the CCSO the minimum oxygen flow rate is, $F_{(O_2)} = (8/3)(m_c/t_r \cdot \rho_{(O_2)})$ where m_c the carbon weight in the mixture in grams, t_r the total reaction time in minutes, $\rho_{(O_2)} = 1.429\ kg/m^3$ the oxygen density under normal conditions. Thus, the minimum oxygen flow needed for complete conversion of