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Simple recipe to synthesize single-domain $BaFe_{12}O_{19}$ with high saturation magnetization

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ABSTRACT

We report a new synthesis route for preparation of single-domain barium hexaferrite ($BaFe_{12}O_{19}$) particles with high saturation magnetization. Nitric acid, known as a good oxidizer, is used as a mixing medium during the synthesis. It is shown that formation of $BaFe_{12}O_{19}$ phase starts at 800 °C, which is considerably lower than the typical ceramic process and develops with increasing temperature. Both magnetization measurements and scanning electron microscope micrographs reveal that the particles are single domain up to 1000 °C at which the highest coercive field of 3.6 kOe was obtained. The best saturation magnetization of $\approx$60 emu/g at 1.5 T was achieved by sintering for 2 h at 1200 °C. Annealing at temperatures higher than 1000 °C increased the saturation magnetization, on the other hand, decreased the coercive field which was due to the formation of multi-domain particles with larger grain sizes. It is shown that the best sintering to obtain fine particles of $BaFe_{12}O_{19}$ occurs at temperatures 900–1000 °C. Finally, magnetic interactions between the hard $BaFe_{12}O_{19}$ phase and impurity phases were investigated using the Stoner–Wohlfarth model.

1. Introduction

Barium hexaferrite ($BaFe_{12}O_{19}$) has been widely used as a permanent magnet due to its very beneficial features like high magnetocrystalline anisotropy with single magnetization axis, relatively high saturation magnetization, high Curie temperature and excellent chemical stability. Fine particles (submicron grain size) of this hexaferrite are one of the most commonly used materials in magnetic recording applications [1] and have ability to absorb electromagnetic radiation in microwave range [2]. For a better performance, coupling between the magnetic grains should be decreased which can be achieved by synthesizing finer single-domain particles with narrow size distribution. In other words, magnetic properties of this material depend mostly on its microstructure which is very much affected by preparation conditions.

Conventional solid-state reaction route, unfortunately, is not suitable for this purpose (i.e., preparation of fine particles), since it requires sintering at relatively high temperatures ($>$1200 °C) and generally results in formation of multi-domain structures which requires repeated grinding and milling. In this case, a certain level of contamination in the final product cannot be avoided.

Several preparation techniques have been used in recent decades to have better structural and magnetic properties of this material. For instance, co-precipitation [3], hydro-thermal [4], sol–gel [5], glass crystallization [6] and low-temperature combustion [7] are among these techniques. In our previous work, we have successfully applied another combustion method to synthesize some oxide materials with better magnetic and superconducting properties at temperatures lower than the solid-state reaction route. The technique is based on dissolution of initial oxides in ammonium nitrate melt (ANM). Some ceramic oxides, including soft magnetic material YIG ($Y_3Fe_5O_{12}$) [8] which is widely used in magneto-optical applications [9–11] and superconductors like YBCO and BSCCO [12,13], were prepared with this method. Using liquid medium to mix initial oxides (or constitutes) on an ionic level is the common point in both ANM and others techniques mentioned above. In this way, the desired phase may be formed by sintering at relatively low temperatures.

In this work, we have used a different mixing medium to prepare fine barium hexaferrite powders. Oxides of the initial powders were mixed in 1 M nitric acid (HNO_3) solution during heating at 100 °C. The precursor, then, calcinated at 450 °C for 4 h to remove organic compounds [14]. The final sintering has been done at temperatures starting from 700 °C to 1200 °C for 2 h. X-ray

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powder diffractometer with CuK_α radiation was used to make phase identification. Particle morphology was studied by scanning electron microscopy (SEM) and magnetic measurements were performed by using a vibrating sample magnetometer (VSM).

Acid catalysts are generally used in the sol–gel method as secondary coordinating agents together with ethylene glycol [14–16]. In the literature, hydrochloric acid (HCl) was also used after the synthesis of barium ferrite powder to remove non-magnetic phases like α-Fe_2O_3 and $BaFe_2O_4$ [17]. Other than these, there is no application of acids in preparation of this material to the best of our knowledge. From this point of view, this work may be the first report which uses only nitric acid as mixing medium to obtain single-domain barium hexaferrite with quite high saturation magnetization. The advantage of mixing in nitric acid solution is that NO_3^- ions form an oxidizing environment which may increase the rate of oxidation. In this way, number of oxygen vacancies can be decreased, and thus, the superexchange interaction of Fe–O–Fe atoms can be enhanced. This may improve the magnetic properties of the barium hexaferrite.

2. Experimental

Appropriate amounts of $BaCO_3$ and Fe_2O_3 powders were weighted to prepare barium hexaferrite in a nominal composition (i.e., Ba:Fe ratio is 1:12). Starting materials were mixed, while heating at 100 °C, in 1 M nitric acid solution (having pH = 0.5) by using magnetic stirrer. For 5 g of initial powders, 100 ml acid was used. During this process, all oxides were converted into the metallic nitrates (i.e., $Ba(NO_3)_2$ and $Fe(NO_3)_3$) through the reactions below. And, one can observe the release of CO_2 in reaction (1) directly.

$$BaCO_3 + 2HNO_3 \rightarrow Ba(NO_3)_2 + CO_2(g) + H_2O \quad (1)$$

$$1/2Fe_2O_3 + 3HNO_3 \rightarrow Fe(NO_3)_3 + 3/2H_2O \quad (2)$$

Mixing was continued until dry precursor was obtained. Before grinding in an agata mortar for 15 min, small amount of ethyl alcohol was added to make wet grinding. Then, the precursor was calcinated at 450 °C for 4 h to remove possible organic compounds. It was reported that, in the presence of NO_3^- ions, formation of non-magnetic phase α-Fe_2O_3 is possible in a wide temperature range. To eliminate this intermediate phase, calcination at 450 °C is very beneficial [14]. Gasses such as NO and NO_2 were also released up to this temperature and metallic nitrates were converted to the oxides again. Finally, the precursor was pelletized under the pressure of 200 MPa before annealing at temperatures from 700 °C to 1200 °C for 2 h which leads to the formation of $BaFe_{12}O_{19}$ phase in two steps. First, hematite (Fe_2O_3) and barium oxide form barium monoferrite ($BaFe_2O_4$) and then $BaFe_2O_4$ reacts with hematite to form barium hexaferrite [18].

The structural properties and fractions of different phases of the samples were investigated using an X-ray powder diffractometer (RigakuMiniflex, Cu-K_α radiation). The surface morphology and microstructure of the samples were examined with a scanning electron microscope (JEOL 6335F, Field Emission Gun). The magnetic characterization of the samples was performed at room temperature using a vibrating sample magnetometer (LDJ Electronics Inc., Model 9600) in an applied field of 15 kOe.

Isothermal remanence (IRM) curves were measured by applying small dc field to the sample and, then, remanent magnetization was measured after the removal of the field. The field was slightly increased to higher value and the process repeated. The procedure was continued until the sample reached the saturation remanent magnetization (M_r).

In order to measure dc demagnetization (DCD) remanence, the sample was initially saturated in some direction and then field was removed to measure $M_d(H=0)$. A small field in opposite direction was applied and removed. The remanent magnetization was measured $M_d(H_1)$. A slightly larger opposite field was applied and removed to measure $M_d(H_2, H_2 > H_1)$. This was repeated until the sample reached to saturation in opposite direction.

3. Results and discussion

3.1. Structural characterization

Phases occurred in samples sintered at different temperatures are shown in Fig. 1. At 700 °C, α-Fe_2O_3 is the main phase and small amount of $BaFe_2O_4$ is also present. When the precursor is sintered at 800 °C for 2 h, $BaFe_{12}O_{19}$ phase starts to form and becomes a major phase with fraction of 0.58, see Table 1. Longer heat

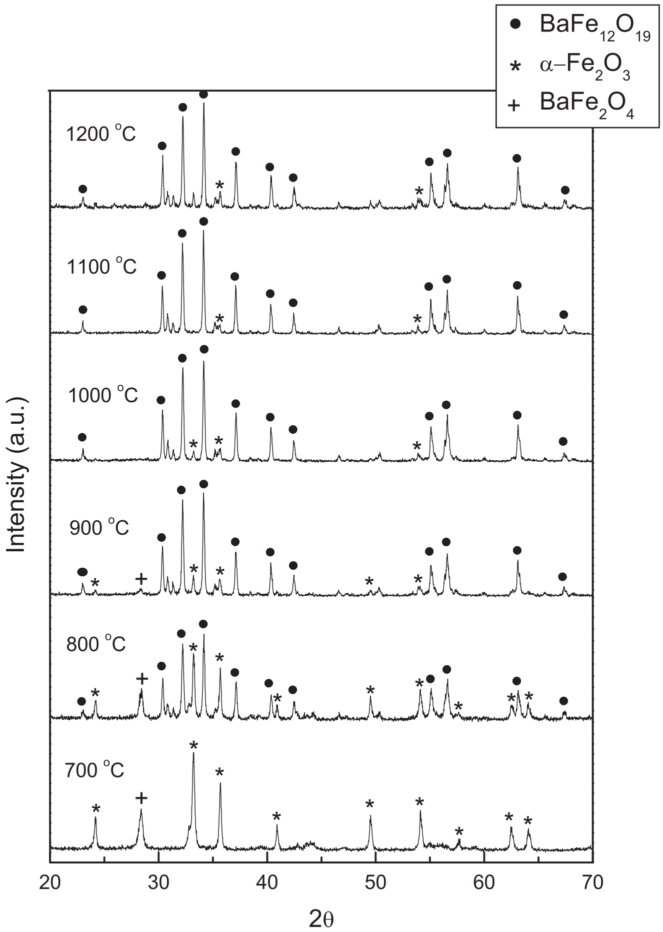

Fig. 1. XRD patterns of the samples sintered at temperatures between 800 and 1200 °C. Peaks corresponding to hard and impurity phases are also marked.

Table 1
Phase fractions of our samples are calculated using the peak intensities of the XRD patterns.

Annealing temperature (°C)	$BaFe_{12}O_{19}$	α-Fe_2O_3	$BaFe_2O_4$
800	0.58	0.37	0.05
900	0.87	0.11	0.02
1000	0.94	0.06	–
1100	0.96	0.04	–
1200	0.93	0.07	–