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Composition and magnetic properties of M-Ba ferrite powders fabricated via sugar-nitrates process

X. TANG[*], Y.G. YANG

State Key Laboratory of OGRGE, Southwest Petroleum University,
No. 8 Xindu Road, Chengdu 610500, P.R. China

Fine M-type hexagonal barium ferrite (M-Ba ferrite) powders were synthesized by a novel sugar-based process. The effects of synthesis variables such as the molar ratio of Fe/Ba, the calcination temperature and the pH value of the precursor solution on the phase component of the obtained powder and the magnetic properties of M-Ba ferrite were studied by the thermogravimetric analysis, differential thermal analysis, X-ray diffraction, scanning electron microscopy and a physical properties measurement system. The results of this study showed that magnetic properties and formation of M-Ba ferrite were significantly influenced by the Fe/Ba molar ratio, the heat treatment temperature and pH of the precursor solution. Single phase M-Ba ferrite powders with the specific saturation magnetization of 63.6 emu/g and the coercivity of 1849 Oe could be obtained when the Fe/Ba molar ratio was 11.5 and the pH value of precursor solution was 6.5.

Key words: *sugar-nitrates process; M-Ba ferrite powder; X-ray diffraction; magnetic properties*

1. Introduction

Barium ferrite with a hexagonal molecular structure is a well-known permanent magnet. It is widely used in magnetic recording media, in microwave devices and as an absorber [1]. The conventional way of producing ferrite is by solid-state reaction of a mixture of $BaCO_3$ and Fe_2O_3, and then calcination at high temperature (higher than 1200 °C). The solid-state reaction method has some inherent disadvantages such as chemical inhomogeneity, coarser particle size, and the contamination with impurities during ball milling. In the last few years, alternative methods, such as chemical co-precipitation [2], precursor technique [3], salt-melt technique [4, 5], hydrolysis of metal-organic complexes [6], etc., have been proposed in order to overcome the limitations of the solid-state reaction method and improve the properties of barium ferrites. As is well known, the method of synthesis strongly affects homogeneity of the product, particle size distribution, shape, and magnetic characteristics [7]. Moreover, the

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[*] E-mail: tungqin@126.com

synthesis parameters are interrelated in a complex way which, in turn, determines the material performance. In the current research, we present a novel, sugar-based process to prepare barium ferrite. Sugar (saccharose) is a carbohydrate, which yields two monosaccharides upon hydrolysis, and the product can easily be further oxidized into carboxylic acid in the presence of an oxidizer. Carboxylic acid is a kind of ligand and forms chelate complexes with many multivalent ions. Therefore, we used white granulated sugar as a chelating agent. A metal nitrates–white granulated sugar solution was used to prepare the precursor of the product, and then the precursor was thermally decomposed and transformed into fine powder of $BaFe_{12}O_{19.}$ In this paper, we report on the synthesis, phase evolution, microstructure, and magnetic properties of barium ferrite. In particular, we discuss the effects of processing parameters such as pH, the molar ratio of Fe/Ba and the calcination temperature on the phase composition and magnetic properties of the resultant barium ferrites powders.

2. Experimental

Synthesis of samples. The chemicals used in this study were of reagent purity and were used without further purification. The starting materials were $Fe(NO_3)_3{\cdot}9H_2O$ (99.9% purity), $Ba(NO_3)_2$ (99.5% purity), white granulated sugar (Shanghai Sugar and Tobacco Industry Limited Company, China, GB317, saccharose >98%) and ammonium hydroxide (concentration: 30 wt. %). For studies on the effect of various Fe/Ba molar ratios, the molar ratio of Fe/Ba was set to 10.9, 11.5, and 12.0 which are denoted as A1, A2 and A3, respectively. The chemicals were weighed and dissolved in a minimum quantity of water (120 cm^3 for 0.1 mol of Fe^{3+}). Ferric nitrate and sugar solutions were mixed according to a prespecified proportion (for all the samples, the molar ratio of sugar to metal ions was set to 3/2) and barium nitrate was added with continuous stirring for 2 h. Then the mixed solution was evaporated slowly at 90 °C, during which the Fe^{3+} and nitrate ions provided an in situ oxidizing environment for the sugar to be hydrolyzed and converted into carboxylic acids. The nitrates themselves were decomposed with the evolution of brown fumes of nitrogen dioxide. Then the obtained solution was cooled. Solutions with various pH values can be obtained by introducing appropriate amounts of ammonia solution. The precursors were precipitated and separated from the reaction medium by adding ethanol. The shallow green precipitate was then filtered and dried at 80 °C for 24 h to become a dry precursor. Finally, powders of the dried precursors were heat treated in air at various temperatures at the heating rate of 10 °C/min to obtain barium ferrite phase.

Characterization. The thermal decomposition of the dried powders was examined by the DTA/TGA in air using a TA Instruments TGA2050 thermo-gravimetric analyzer with the heating rate of 20 $°C{\cdot}min^{-1}$. The X-ray powder diffraction pattern data of the samples were collected by an X-ray diffractometer (Philips X'pert Pro PW3040) set to a wavelength of 1.54051 Å of CuKα radiation in the 2θ range 20–80°. The morphology of particles was examined with a Philips Siron 200 field emission type scanning electron microscope (FE-SEM). The magnetic properties of some selected specimens were measured by means of a physical properties measurement system (PPMS-9, USA) at a maximum applied field of 30 kOe at room temperature.

3. Results and discussion

The TGA and DTA curves recorded in air for the dried precursor with the Fe/Ba molar ratio of 11.5 and a pH of 6.5 are shown in Fig. 1, as a typical example. All other samples show a similar thermal behaviour. The TGA pattern exhibits three distinct weight loss steps corresponding to an endothermic peak and two exothermic peaks in the DTA curve.

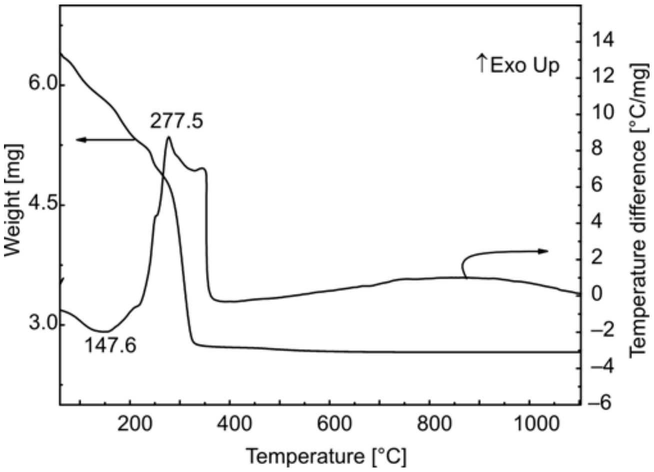

Fig. 1. DTA/TG curves of the dried precursor with the Fe/Ba molar ratio of 11.5 and pH value of 6.5

On heating we observe a continuous mass loss in the TG curve between room temperature and 250 °C which is accompanied by a distinct endothermic peak around 147.6 °C in the DTA curve, ascribed to the vaporization of residual water molecules; a more pronounced mass loss between 250 °C and 350 °C is associated with the release of large quantities of gas, the DTA analysis indicated a large exothermic double peak at 250–350 °C, which is caused by the release of a large amounts of heat due to vigorous oxidation reaction or combustion reaction of carbonaceous residue. The whole thermal process is accompanied by the evolution of large amounts of gas that is manifested in the weight loss in the TG curve. The exothermic temperature in the DTA pattern is consistent with the major weight loss temperature in the TGA pattern. No further distinguishable weight change above 350 °C is observed, though there is a broad exothermic peak around 800 °C, due to the crystallization process of phase transformation.

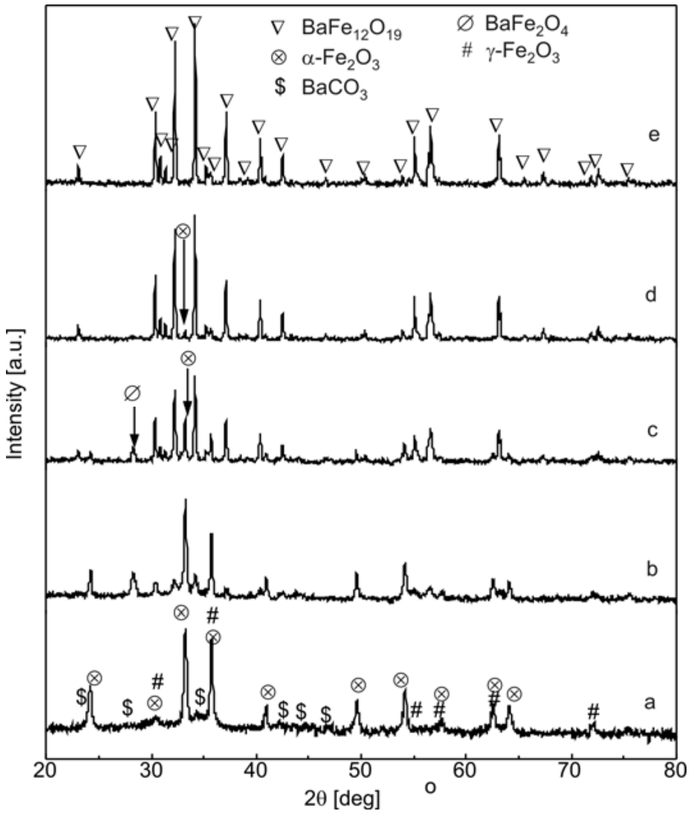

Fig. 2. XRD patterns of calcination powders at:
a) 400 °C, b) 650 °C, c) 850 °C, d) 1000 °C, e) 1100 °C

Figure 2 shows the X-ray powder diffraction patterns of the specimens with the molar ratio of Fe/Ba = 11.5 annealed at various temperatures. It is evident that the powder annealed at 400 °C mainly shows a mixture of phase α-Fe_2O_3, γ-Fe_2O_3 and $BaCO_3$. As temperature reached 650 °C, the intensity of γ-Fe_2O_3 decreases markedly, and $BaCO_3$ phase disappeared, the $BaFe_{12}O_{19}$ (JCPDS No. 74-1121) and intermediate phase identified as barium iron oxide ($BaFe_2O_4$) were formed. In the 850–1000 °C temperature range, $BaFe_{12}O_{19}$ was the major phase with a small amount of residual α-Fe_2O_3. Pure $BaFe_{12}O_{19}$ was formed at 1100 °C. It is in disagreement with the results by Pullar et al. [8] where the single phase barium ferrite can be easily formed directly in sol-gel systems, where no $BaCO_3$ is involved, and without formation of an intermediate phase. In this study, α- and γ-Fe_2O_3 co-exist in the intermediate phase in pattern (a), α-Fe_2O_3 has $FeTiO_3$-type structure, which belongs to the trigonal crystal system difficult to transform into the $BaFe_{12}O_{19}$ phase, a complete conversion of the mixture into single $BaFe_{12}O_{19}$ phase requires a high temperature.

Figure 3 shows the SEM micrograph of the specimens synthesized with the Fe/Ba molar ratio of 11.5 and calcined at 1100 °C for 2 h. From the image it can be seen that the sample consists of various morphologies, i.e., it shows small amounts of spherical particles and a greater number of platelets, aggregated and joined by weak bonding. As shown in the SEM micrograph, barium ferrite powders annealed at 1100 °C exhibit aggregates with an irregular shape and particle coarsening and sintering.

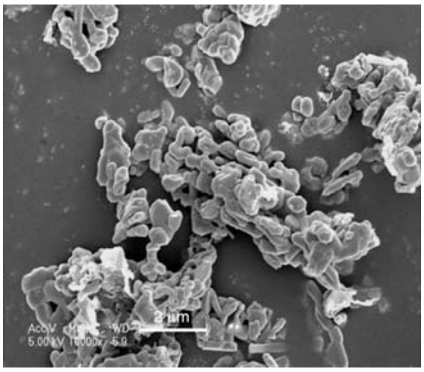

Fig. 3. SEM micrograph of the sample with the Fe/Ba molar ratio of 11.5, calcined at 1100 °C for 2 h

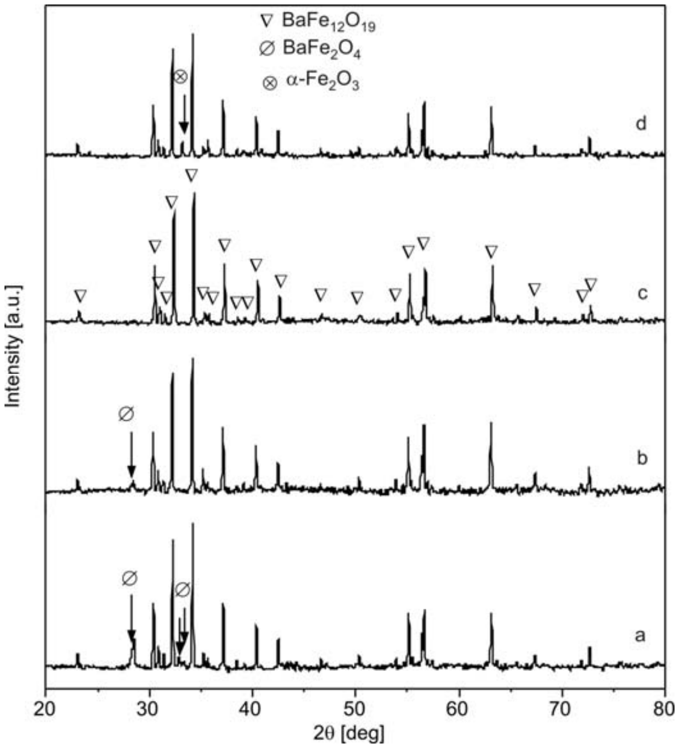

Fig. 4. X-ray diffraction patterns of powders derived from the sugar-nitrate process with various pH values of the precursor solution: a) 1.2, b) 4.0, c) 6.5, d) 9.0

The influence of pH of the precursor solution on the chemical composition of the sugar-based derived barium ferrite powders can been seen in Fig. 4, which shows the

XRD patterns of the specimens after having been thermally treated at 1100 °C for 2 h. The heated specimens with a Fe/Ba ratio of 11.5 were prepared using precursor solution of different pH values (i.e., pH = 1.2 (without any NH_4OH addition), 4.0, 6.5 and 9.0, respectively). Barium ferrite was the major phase in all specimens, however, pure barium ferrite was obtained at pH = 6.5. Small amounts of α-Fe_2O_3 or $BaFe_2O_4$ crystallites were detected at pH of 1.2, 4.0 and 9.0. As previously indicated, sugar yields two monosaccharides upon hydrolysis, and the product can easily be further oxidized to carboxylic acid in the presence of an oxidizer. Carboxylic acid is a kind of ligand and complexes with many multivalent ions to form chelates. Bechtold et al. [9] described the complexation of Ca^{2+} ions by the Fe–D-gluconate system, and the species distribution calculated for the system $Ca^{2+}Fe^{3+}$DGI is shown in Fig. 5.

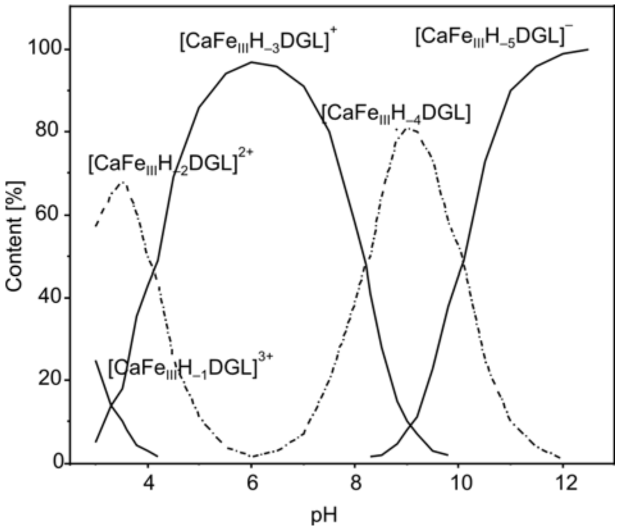

Fig. 5. Species distribution calculated for the system $Ca^{2+}Fe^{3+}$DGI [9]

In this case, gluconic acid molecules, with a carboxylic acid group at one end and five linear hydroxyl groups, easily form metal ion complexes in the complex system of Ba-Fe-gluconic acid. As described in the literature, the formation constants, species distribution and stoichiometry of the complexes are dependent on pH of the solution. It is believed that the complex species resulting from chelation of metallic ions in the solution is responsible for the phase composition of the resultant powders. Upon heating, the specimen prepared from the solution of pH = 6.5 can easily and completely convert to hexagonal barium ferrite.

The saturation magnetization (M_s), remanent magnetization (M_r) and coercivity (H_c) of barium ferrite particles at various pH are shown in Table 1. When the pH of the precursor solution is 6.5, the particles are single phase $BaFe_{12}O_{19}$, exhibiting better magnetic properties than those obtained at other pH values. It is believed that chemical phases present in the specimens are the main reason for small differences in the values of saturation magnetization. Magnetic data are in good agreement with the results obtained from XRD.

Table 1. Magnetic properties of calcined powders
for various pH values of the precursor solution

pH	M_s [emu/g]	M_r [emu/g]	H_c [Oe]
1.2	52.8	27.5	2476.3
4.0	58.4	30.8	2502.8
6.5	62.2	31.5	2546.5
9.0	55.5	28.6	2396.3

It is worthwhile to point out that these values of magnetic saturation are high, although they are lower than the theoretical one (72 emu/g). On the other hand, the coercivity values for the products are lower than those obtained for barium ferrite powders produced by coprecipitation [10]. It is unlikely that the lower coercivity were a result of the presence of small amounts of amorphous impurities, undetectable by XRD: it is far more likely that the intrinsic properties of the prepared powders are responsible. The higher saturation magnetization and the lower coercivity have potential applications in microwave absorption and in high-density magnetic recording. As is well known, the magnetic properties are influenced by many factors such as the grain size and particle size distribution, morphology and microstructure of particles, the method of synthesis, etc. According to our SEM image (Fig. 3), the particle shape was not an ideal hexagon and plate-like. Also, evident agglomeration occurred. In our opinion, the non-equilibrium microstructure and the uniform size of the particles should be the main reasons for those low coercivity values, and, in addition, the method of synthesis might be another reason. More evidence may be required to understand the present results of measurements.

Figure 6 shows the XRD patterns of the specimens obtained at various Fe/Ba molar ratios. Table 2 shows their magnetic properties. Single phase M-type $BaFe_{12}O_{19}$ powders with better magnetic properties were obtained at the Fe/Ba ratio of 11.5. On the other hand, the XRD patterns showed that formation of the mono-ferrite $BaFe_2O_4$ took place at the Fe/Ba molar ratio of 10.9 and of α-Fe_2O_3 at the Fe/Ba molar ratio of 12.0. Owing to their antiferromagnetic character, the α-Fe_2O_3 or $BaFe_2O_4$ intermediate phases deteriorate the magnetic properties. The appropriate molar ratio of Fe/Ba may vary with the fabrication method used and the starting materials. Liu et al. [11] suggested that the Fe/Ba molar ratio of 8 is a favourable one in order to obtain single phase M-type $BaFe_{12}O_{19}$. An investigation of the synthesis of barium ferrite by coprecipitation showed that the M-type phase only forms as a pure product in a non-stoichiometric mixture with a Fe/Ba =11 [12]. On the other hand, single phase barium ferrite can be obtained from a stoichiometric mixture of Fe/Ba = 12 via a sol-gel route [13]. Usually, an iron deficient non-stoichiometric mixture with the excess barium is needed to form the single-phase product.

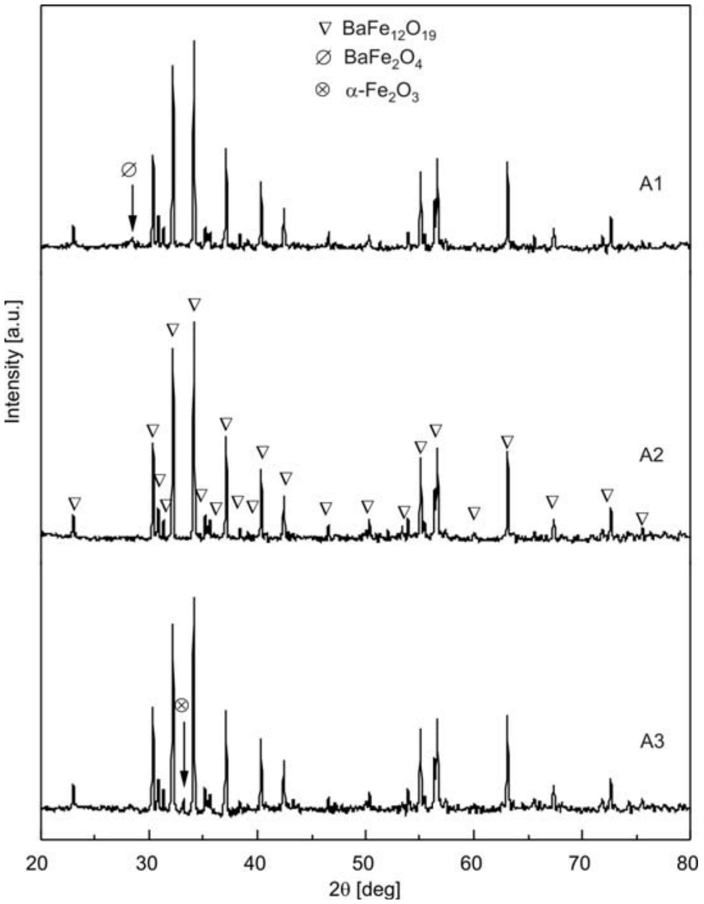

Fig. 6. XRD patterns of powders calcined at 1100 °C for 2 h at various starting Fe/Ba molar ratios

Table 2. Magnetic properties of calcined powders for various Fe/Ba molar ratios

Fe/Ba molar ratio	M_s [emu/g]	M_r [emu/g]	H_c [Oe]
10.9	56.3	30.6	1649.5
11.5	64.5	33.8	1848.9
12.0	54.5	26.9	1785.2

In our study, it seems that the Fe/Ba molar ratio of 11.5 is more favourable than other ratios for the formation of single phase barium ferrite. In the case of chemical synthesis routes, it has been proposed that a deviation from $BaFe_{12}O_{19}$ stoichiometry should be considered due to variations in the solubility of the Fe^{3+} and Ba^{2+} cation sources. This can be accounted for by the fact that the solubility of Ba nitrate in water is poor, and the coordinative ability of carboxylic acid to the Fe^{3+} cation is much stronger than that of carboxylic acid to the Ba^{2+} cation. Ba nitrate can crystallize from precursor solution during evaporation [14]. The other reason is attributed to enhanced diffusion rates among various ions in the non-stoichiometric mixtures due to induced lattice defects permitting single-phase formation at a lower temperature [15]. Similar to the other synthesis routes, it is noticeable that an excess amount of barium ions is required in order to keep the stoichiometry for barium ferrite in the sugar-nitrates process.

4. Conclusions

Using $Fe(NO_3)_3{\cdot}9H_2O$, $Ba(NO_3)_2$ and white granulated sugar as the starting materials, fine M-type barium ferrite powders were synthesized successfully by the sugar nitrates process. The crystal structure and magnetic properties of the prepared powders were investigated. The results show that the annealing temperature, the molar ratio of Fe/Ba and pH of the precursor solution affected greatly the phase composition and magnetic properties of M-Ba ferrite powders. Single phase M-type barium ferrite powders with superior magnetic properties were obtained at the Fe/Ba molar ratio of 11.5 and pH = 6.5. The powders exhibited higher values of saturation magnetization and lower coercivity. These features of the prepared powders point to their potential applications in microwave absorbing and in high-density magnetic recording.

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