MAGNETIC PROPERTIES OF AEROSOL SYNTHESIZED BARIUM FERRITE PARTICLES

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Abstract

Barium ferrite fine particles have been synthesized from ferric nitrate and barium nitrate aqueous solution by an aerosol technique. The as-received particles showed a spin glass behavior with a history-dependent low-field magnetization below 180 K. An exothermic peak with initial crystallization temperature of 687°C was found by DSC analysis. Heat treatments above this temperature dramatically changed the magnetic properties and morphologies without changing the Ba/Fe atomic ratio which was 1/12. Heat treated samples had coercivities and saturation magnetization as high as 5360 Oe and 70.6 emu/g, respectively.

Introduction

Barium ferrite fine particles have been considered to be a promising material for high density vertical magnetic recording [1]. The conventional method of preparation of these particles has been to sinter appropriate mixtures of iron oxide with barium oxide at high temperature [2]. Other techniques, such as the glass crystallization method [2], the liquid-mix technique [4], and colloidal method [5] have been also used.

Application of an aerosol technique in material synthesis is a promising subject. We have successfully used such a technique to make iron oxide fine particles [6]. Our technique has two main advantages in synthesizing fine particles. First, materials are mixed in solution hence they are mixed at the start on the atomic level. Second, only subsintering temperatures are necessary to form crystallized particles.

Experimental Methods

An aerosol generator as described elsewhere [6] was used to synthesize the fine particles. $Fe(NO_3)_3.9H_2O$ and $Ba(NO_3)_2$ were dissolved in distilled, deionized water with a Fe/Ba atomic ratio of 12 to a concentration of 2% wt. This solution was fed to a constant output atomizer (Model 3075, TSI, St. Paul, MN) operated by a nitrogen gas flow of 2.6L/min at a pressure of 35 psig. The liquid drop aerosol stream passed through a diffusion dryer to remove water and then was heated to 800°C as it passed through a tube furnace. The aerosol particles were collected on cover glasses by thermophoresis after they passed through the tube furnace. Powder samples were obtained by scraping the particles off the cover glasses. Further heat treatment was also made in a nitrogen environment at 800°C.

A SQUID magnetometer was used to measure the magnetic properties and other techniques such as TEM, DSC, and x-ray diffraction were also used to characterize the particles.

Results and Discussions

The as-received sample had a residence time t_s of 1.4 seconds defined as the passage time through the 800°C tube furnace. This sample showed low saturation magnetization (7.1 emu/g at 300 K) compared to that of bulk barium ferrite (72 emu/g). The coercivity was 6100 Oe at 10 K, but it was decreased to 200 Oe at 300 K. This rapid change led us to measure the temperature dependence of the magnetization which is shown in Figure 1. Curves are normalized to their magnetization at 300 K ($\sigma_{300\ K}$). The magnetization exhibited a cusp at 180 K when the sample was zero-field cooled (ZFC) and then measured in a field of 400 Oe. This cusp was almost flattened with field cooling (FC) at 400 Oe and totally disappeared at 10^4 Oe field cooling.

Even though the Fe/Ba atomic ratio of the as-received sample as detected by EDXA was very close to that of barium ferrite ($BaFe_{12}O_{19}$), the x-ray diffraction showed an amorphous phase. This amorphous state was corroborated by DSC measurements which are shown in Figure 2. An exothermic peak centered at 710°C, with 20°C/min heating rate, indicated the onset of crystallization beginning at 687°C.

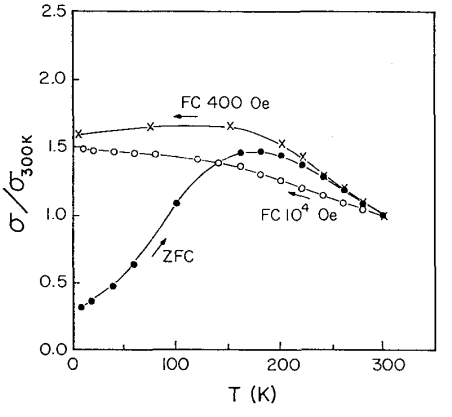

Fig. 1 Magnetization (normalized to $\sigma_{300\ K}$) as a function of temperature in zero-field cooled and field cooled as-received samples.

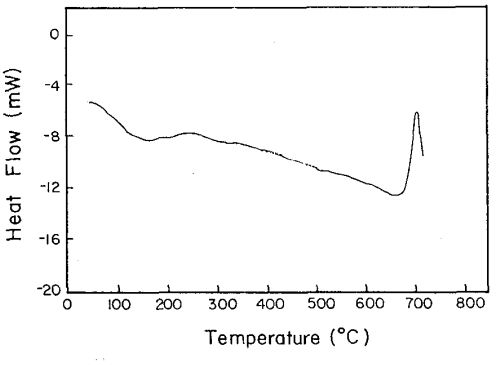

Fig. 2 DSC measurements on as-received sample.

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The amorphous characteristics of the as-received sample is the result of our aerosol preparation technique. Iron and barium nitrate molecules were randomly distributed in the aqueous solution. This random structure remained in the particles even after the diffusion dryer removed H_2O and the tube furnace decomposed the iron nitrate and barium nitrate mixture to a phase in the form of Ba-Fe-O. The 1.4 seconds residence time, however, must not be long enough to crystallize this amorphous state.

Further heat treatment was needed to turn these amorphous particles to crystallized barium ferrite. This treatment was also done in a nitrogen environment. Figure 3 shows the saturation magnetization (σ_s) and coercivity (H_c) as functions of the annealing temperature (T_a). The annealing time was chosen to be 1 hour. No change was detected below 600°C for the saturation magnetization. Samples experienced a dramatical change in saturation magnetization between 600°C and 800°C. At 700°C, σ_s was 64.6 emu/g which was 90% of that of bulk barium ferrite at 300 K. These results are in good agreement with the DSC results which showed beginning near this crystallization temperature. A sample annealed at 1000°C reached a saturation magnetization of 70.6 emu/g (at 300 K) which was within experimental error of the bulk value.

When the annealing temperature was below 600°C, the coercivity measured at 10 K decreased with annealing temperature while it increased with annealing temperature when measured at 300 K. The coercivity at room temperature was much lower than that at 10 K because of thermal agitation. An enhanced change also occurred for the coercivity between 600°C and 800°C. The two temperature curves intersect at about 680°C and thereafter the coercivity at 300 K was higher than that at 10 K, which is consistent with Mee and Jechke [7]. The highest coercivity (5360 Oe) was obtained with an annealing temperature of 1000°C.

Experiments to study the effect of annealing time were also performed in a nitrogen environment. We chose 800°C as the annealing temperature which was higher than the crystallization temperature. Figure 4 shows saturation magnetization and coercivity as functions of annealing time. Saturation magnetization increased with annealing time monotonically. Even at t_a as short as 20s, σ_s had reached 91% of the bulk value and the two curves of coercivity as measured at 10 K and 300 K intersected. At long annealing time samples showed high magnetization and high coercivity.

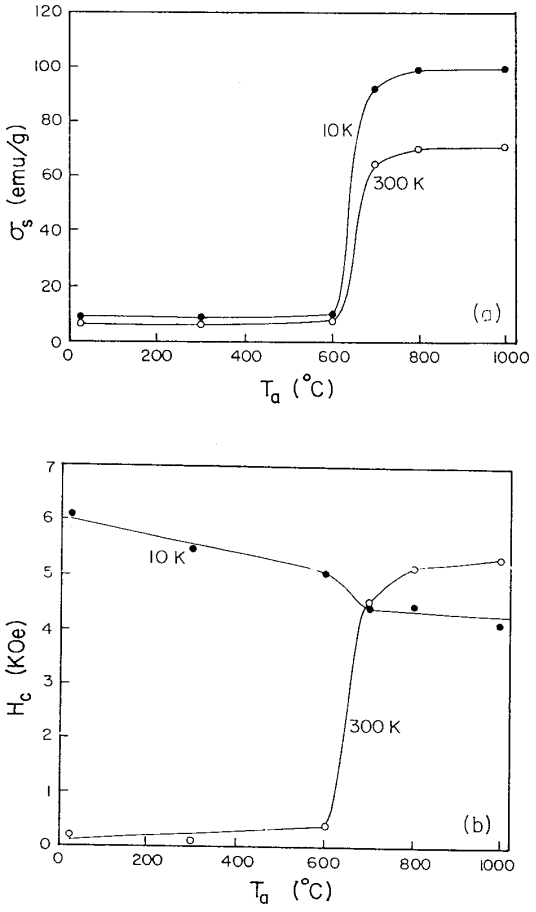

Fig. 3 Saturation magnetization (a) and coercivity (b) as functions of annealing temperature (T_a) in a N_2 atmosphere. The annealing time was 1 hour.

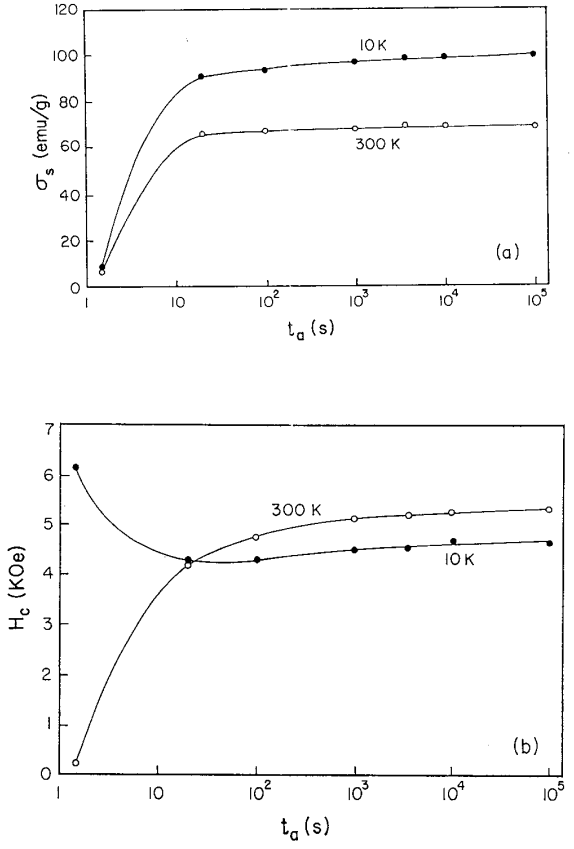

Fig. 4 Saturation magnetization (a) and coercivity (b) as functions of annealing time (t_a) at 800°C in a N_2 atmosphere.

While heat treatment did not change the Fe/Ba atomic ratio which was 12/1, as detected by EDXA, the particle microstructure and morphology were changed. The amorphous state existed in the as-received sample. X-ray diffraction studies, however, showed clearly a single barium ferrite ($BaFe_{12}O_{19}$) phase in the heat treated samples. TEM was used to study the particle morphology. The as-received sample had a broad distribution of spherical particles with an average diameter of 800Å (Fig. 5a). Heat treatment changed these spherical particles to platelet-shaped particles (Fig 5b) which are typical for barium ferrite. These platelet-shaped particles had an average thickness of 400Å with aspect ratio of 3.5.

Conclusion

Amorphous Ba-Fe-O fine particles with magnetic properties characteristic of spin glass have been prepared by an aerosol technique. Subsequent heat-treatments turned these particles to the barium ferrite crystalline ($BaFe_{12}O_{19}$) phase. Both annealing temperature and annealing time evolution of magnetic properties showed a simple transition from the amorphous state to the crystallized state.

Acknowledgements

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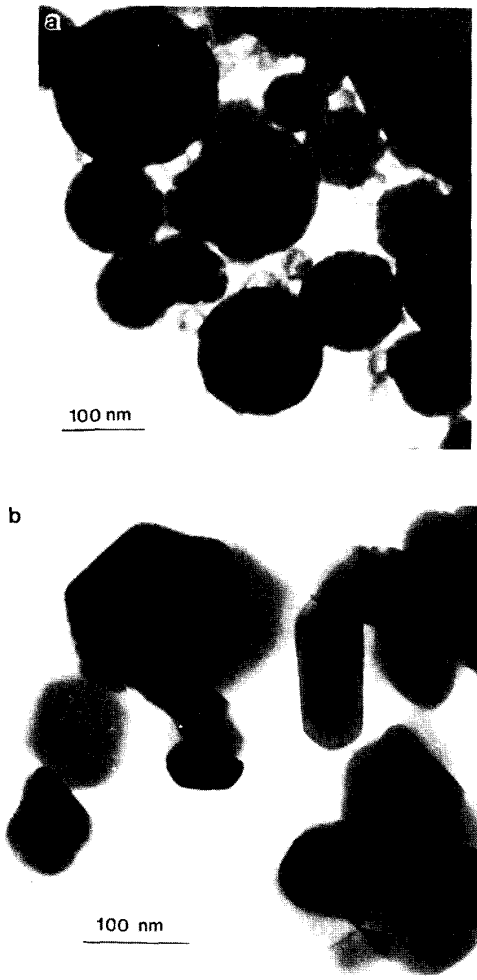

Fig. 5 Transmission electron micrograph (a) as-received sample, (b) heat-treated sample.