Preparation of nanoparticles of barium ferrite from precipitation in microemulsions

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Abstract

Magnetic nanoparticles of barium ferrite ($BaFe_{12}O_{19}$) have been synthesized using a microemulsion mediated process. The aqueous cores of water-in-oil microemulsions were used as constrained microreactors for the precipitation of precursor carbonate and hydroxide particles. These precursors were then calcined at 925°C for 12 h, during which time they were transformed to the hexagonal ferrite. The pH of reaction was varied between 5 and 12, and it was found that the fraction of non-magnetic hematite (α-Fe_2O_3) in the particles varied with the pH of reaction, thus affecting the magnetic properties of the particles. The same precursor particles were also prepared by bulk co-precipitation reaction for comparison. It was found that the microemulsion derived nanoparticles of barium ferrite had both higher intrinsic coercivity (H_c) and saturation magnetization (σs) than the particles derived from bulk co-precipitation. Particles were analyzed by electron microscopy, X-ray diffraction, differential thermal analysis (DTA), thermogravimetric analysis (TGA) and vibrating sample magnetometry (VSM). The best barium ferrite particles produced by the microemulsion synthesis method yielded an intrinsic coercivity of 4310 Oe and a saturation magnetization of 60.48 emu/g.

Keywords: nanoparticles, magnetic materials, microemulsions, barium ferrite

Introduction

Recording media requirements

The use of ultrafine magnetic media in the magnetic recording industry has long been recognized as a performance advantage. For optimum performance, recording media must contain small discrete magnetic units that are at least partially independent of each other, so that the transitions between different directions of magnetization in the recorded pattern are stable and not free to move around. Each magnetized segment in the written record must contain a large number of these units, in order that the signal-to-noise ratios be adequate (Mallinson, 1974). It is clearly advantageous, then, for these units to be as small as practical.

If the magnetic units correspond to physical grains or particles, a further reason exists for making them as small as possible. This is the need for a smooth tape or disk surface. The effectiveness of both the recording and reading processes depends critically on minimizing the separation of the head from the medium, which in turn depends at least partly on the smoothness of both (Wallace, 1973; Betram & Niedermeyer, 1982). However, the benefits of very small magnetic switching units must be balanced against a factor that places a lower practical limit on their size. This is the need for adequate stability of the magnetization against the randomizing effects of thermal energy. Extremely small units would exhibit superparamagnetic behavior, having no stable magnetization (Bean & Livingston, 1959). In the particulate recording industry, it is thus desirable to produce monodisperse particles that are large enough to withstand the randomizing effects of thermal energy while still being small enough to be entirely single domain.

Barium ferrite

Besides the effects of particle size which greatly influence the behavior of particulate recording systems, it is obviously desirable to use particles with optimum magnetic characteristics. Barium ferrite ($BaFe_{12}O_{19}$) has traditionally been used in permanent magnets due to its high intrinsic coercivity and fairly large crystal anisotropy (Cullity, 1972). However, there has recently been increasing interest in the use of barium ferrite in the recording industry, with emphasis on the application to perpendicular recording (Kubo & Yokoyama, 1982). The physical and magnetic properties of barium ferrite are generally very desirable. Its chemical stability is excellent, and its switching field distribution is exceptionally narrow. This distinguishing characteristic of barium ferrite may be due to the large magnetocrystalline anisotropy, or may result from a cooperative behavior of particles that have formed a stack (Speliotis, 1987). In any case, barium ferrite has been accepted as a leading material for perpendicular recording applications.

The classical ceramic method for the preparation of barium ferrite consists of firing mixtures of iron oxide and barium carbonate at high temperatures (≈1200°C). Furthermore, the ferrite must then be ground to reduce the particle size from multidomain to single domain. This generally yields mixtures which are nonhomogeneous on a microscopic scale. Milling introduces lattice strains in the materials, which often result in particles with lowered magnetic properties such as saturation magnetization and intrinsic coercivity (Kojima, 1932; Bye&Howard, 1971). However, recent advances in particle production have been applied to the production of barium ferrite particles, and they are now available in a range of sizes and shapes. These techniques include chemical co-precipitation (Mee & Jeschke, 1963; Haneda et

al., 1974; Roos, 1980), glass crystallization (Shirk&Buessem, 1970), organometallic precursor method (Licci & Besagni, 1984; Vallet et al., 1985), colloidal synthesis (Matijevic, 1987) and aerosol synthesis (Tang et al., 1989; Kaczmarek, 1991). However, the preparation of monodisperse particles of barium ferrite in the nanoparticle regime (<0:1µm) remains a challenge. In this paper, an investigation into the preparation of barium ferrite nanoparticles through the use of water-in-oil microemulsions is reported, along with a comparison of the particles produced by this method to particles produced from a bulk co-precipitation method.

Microemulsions

A microemulsion may be defined as a thermodynamically stable dispersion of two immiscible liquids consisting of microdomains of one or both liquids stabilized by an interfacial film of surface active molecules (de Gennes & Taupin, 1982; Leung et al., 1981). In water-in-oil microemulsions, the aqueous phase is dispersed as microdroplets (typically 10–25 nm in size) surrounded by a monolayer of surfactant molecules in the continuous hydrocarbon phase. If a soluble metal salt is incorporated in the aqueous phase of the microemulsion, it will reside within the aqueous droplets surrounded by oil. These microdroplets continuously collide, coalesce and break again (Eicke et al., 1976). If two identical microemulsions are produced with reactant A dissolved in the aqueous cores of one microemulsion and reactant B in the other microemulsion, upon mixing, they will form precipitate AB, which will be contained entirely within the aqueous cores of the microemulsions. The growth of these particles in microemulsions is suggested to involve inter-droplet exchange and nuclei aggregation (Fendler, 1987; Sugimoto, 1987). In the past, this water-in-oil microemulsion technique has been used to synthesize

various nanoparticles including colloidal metals (Boutonnet et al., 1982), silver halides (Hou & Shah, 1988; Chew et al., 1990) and oxalate precursors for YBa2Cu3O7−x superconductors (Ayyub et al., 1990). Recently, this laboratory has applied water-inoil microemulsions to the synthesis of various magnetic materials as well. Previous work has been published reporting the synthesis of both barium ferrite (Pillai et al., 1992, 1993) and cobalt ferrite (Pillai & Shah, 1996; Pillai et al., 1995; Palla & Shah, 1997) in microemulsion.

Experimental procedure

Microemulsion precipitated particles

The microemulsion system chosen to produce barium ferrite nanoparticles from microemulsion synthesis consisted of cetyl trimethylammonium bromide (CTAB) as the surfactant, 1-butanol as the cosurfactant, n-octane as the continuous oil phase and an aqueous solution as the dispersed phase. The microemulsion composition was chosen as to maximize the amount of salt which may be dissolved in the aqueous phase while still producing a clear mixture. The composition of the microemulsion chosen is given in Table 1.

Two microemulsions of identical composition given in Table 1 but with different aqueous phase reactants were prepared for the production of each powder. In microemulsion I was dissolved a mixture of ferric nitrate ($Fe(NO_3)_3$) and barium nitrate ($Ba(NO_3)_2$) in a molar ratio of 12 : 1.1. The desired Fe^{3+} : Ba^{2+} ratio in the product is 12 : 1, so the slight excess of Ba^{2+} in the reactants accounts for the slight solubility of the precipitated barium carbonate particles. In microemulsion II was dissolved sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3) in a weight ratio of 5 : 1, which was

found previously to produce the optimum barium ferrite phase in the co-precipitation scheme used here. These two microemulsions were then mixed under constant stirring, allowing the reacting species to come in contact with each other due to the dynamic nature of the dispersed droplets. This lead to precipitation of precursor hydroxide and carbonate particles within the aqueous microdroplets. The surfactant layer around each droplet acted as a barrier restricting the growth of the particles beyond the water domains. The production of the hydroxide/carbonate precursors by this microemulsion method is illustrated in Figure 1.

Table 1. Composition of the microemulsion system used in all nanoparticle preparations (wt. fraction)

Aqueous phase	0.206
n-Octane	0.529
1-Butanol	0.120
Cetyl trimethyl ammonium bromide	0.145

The precursor precipitate was separated in a super-speed centrifuge at 10 000 rpm for 10 min. The precipitate was then washed in a 1 : 1 mixture of methanol and chloroform followed by 100% methanol to remove residual octane and surfactant from the particles. The particles were then dried at 100°C. The desired ferrite phase was then obtained by calcining the particles for 12 h at 925°C for complete conversion of the precursor particles.

Bulk co-precipitation method

The previous work on barium ferrite production (Pillai et al., 1992, 1993) did not investigate the advantages of microemulsion-derived particles over particles made in bulk processing. In this study, precursor particles were also produced from bulk co-

precipitation. The same reactants were used at the same concentrations for this purpose, except that the reaction was done in aqueous solution with no microemulsion present. These particles were also separated in a superspeed centrifuge at 10 000 rpm for 10 min, but no washing steps were taken since no oil or surfactant was present in the system. The use of microemulsions to produce particles alters the particle size and homogeneity of the particles, while the co-precipitation method does not utilize constrained microreactors in producing the particles and hence produces particles with a larger particle size and a broader particle size distribution. The differences between particles produced by both methods is illustrated schematically in Figure 2.
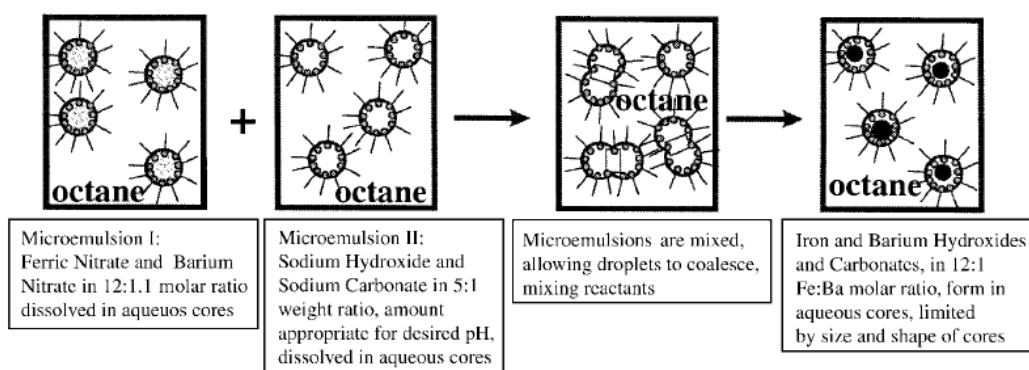

| Microemulsion I: Ferric Nitrate and Barium Nitrate in 12:1.1 molar ratio dissolved in aqueuos cores | Microemulsion II: Sodium Hydroxide and Sodium Carbonate in 5:1 weight ratio, amount appropriate for desired pH, dissolved in aqueous cores | Microemulsions are mixed, allowing droplets to coalesce, mixing reactants | Iron and Barium Hydroxides and Carbonates, in 12:1 Fe:Ba molar ratio, form in aqueous cores, limited by size and shape of cores |

Figure 1. Production of barium and iron hydroxide/carbonate precursor particles from precipitation in microemulsion.
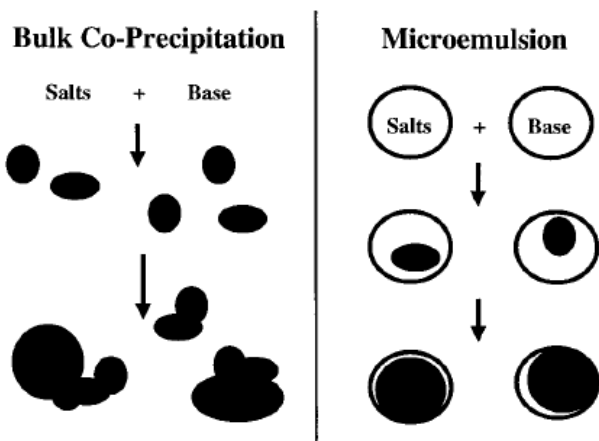

Figure 2. Illustration of particle production by microemulsion synthesis and bulk co-precipitation methods, showing differences in particle size and size distribution obtained.

Variation of pH of reaction

The previous work on barium ferrite production (Pillai et al., 1992, 1993) did not investigate the effects of pH of reaction on magnetic properties. The pH of the reaction taking place upon mixing microemulsionswas varied in this study. Results suggest that the production of the appropriate barium ferrite phase is dependent upon reaction pH, and in fact a stoichiometric excess of at least 40% precipitating agent is necessary to produce any particles. This is because at lower stoichiometries, the reaction pH is <2 due to the presence of $Fe(NO_3)_3$, a strong acid. At pH <2 the precursor particles formed are soluble and hence cannot be separated. At higher pHs of reaction the magnetic properties of the sintered particles are dependent on pH due to the production of non-magnetic hematite (α-Fe_2O_3) particles. The amount of hematite impurity in the barium ferrite particles changes with the pH of reaction. In order to determine the pH of reaction resulting from mixing the reactants several studies were carried out varying the reactant concentrations while monitoring the pH in bulk precipitated samples. The results of this study are given in Figure 3, in which reaction pH is given as a function of salt and base concentrations for mixing 20mL of aqueous solution. These same concentrations were used in microemulsions to produce particles at the assumed same pH of reaction. This assumption is valid due to the fact that the droplet size in microemulsions is sufficiently large to cause the properties of the aqueous droplets to mimic the properties of bulk aqueous solutions under the same conditions.

Results and discussion

For the barium ferrite particles produced from microemulsion, transmission electron microscopy (TEM) was used to study the size and size distribution. The

particles were ultrasonically dispersed in methanol prior to depositing them on a TEM grid.ATEM micrograph of the precursor hydroxide/carbonate particles is shown in Figure 4, which shows particles which are fairly monodisperse and in the size range of 3–8 nm.
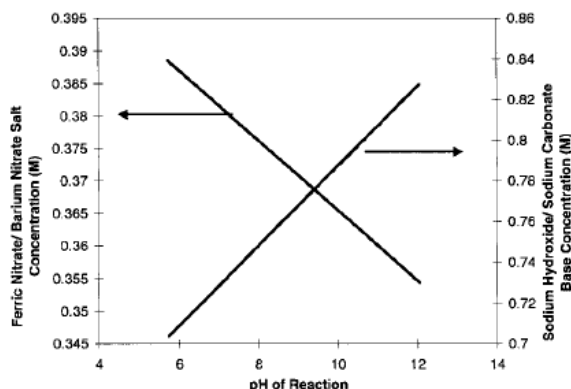

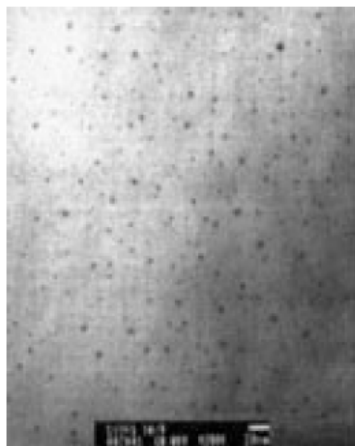*Figure 3.* Concentrations of salt and base solutions needed to achieve desired pH of reaction.

Figure 4. TEM of precursor hydroxide/carbonate particles produced from microemulsion reaction.

A TEM micrograph of calcined barium ferrite particles is shown in Figure 5, which shows that the particles do agglomerate slightly during the calcination step, as expected, but the particle size of the final particles remains less than 0.1 µm. The particles are also free from cracks and other defects which can be expected from conventional processing procedures. X-ray diffraction (XRD) was used to confirm the transition of the precursor to the hexagonal structure of barium ferrite. Figure 6 shows

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XRD patterns for barium ferrite produced at two different pHs of reaction. Figure 6(a) is for particles made at pH 5 and shows peaks for both barium ferrite (B) and hematite (H), while Figure 6(b) is for particles made at pH 10, with only peaks for barium ferrite (B) appearing.
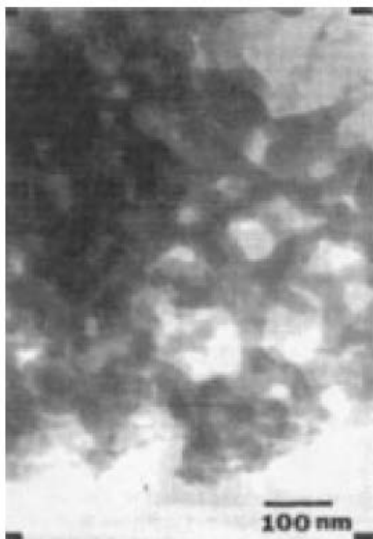
Figure 5. TEM of calcined barium ferrite particles produced from microemulsion reaction.

This confirms that a higher pH of reaction is needed to form the hexagonal structure of barium ferrite. A lower pH of reaction will result in the presence of more hematite (α-Fe2O3), a non-magnetic impurity. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were also applied to the precursor particles to determine the transition temperature for the conversion of the precursor particles to barium ferrite. Figure 7 is the DTA/TGA composite for the sample produced in microemulsion at pH 10. The DTA plot shows an endothermic peak near 650 °C and the TGA plot shows a weight loss in the range of 600–650°C. These peaks are indicative of the transition from precursor to barium ferrite.

Magnetic property measurements

A vibrating sample magnetometer (VSM) was used to obtain magnetic property measurements on particles produced both from microemulsion and from bulk coprecipitation, as a function of pH of reaction. VSM measurements were done on an unoriented, random assembly of particles at room temperature and with a maximum applied field of 16 kOe. For each measurement, a hysteresis loop was generated from which the intrinsic coercivity (H_c) and saturation magnetization (σs) were calculated. Figure 8 is a hysteresis loop obtained for the particles from microemulsion at a reaction pH of 10. Figure 9 is a plot of the intrinsic coercivity obtained for both microemulsion-derived and co-precipitation barium ferrite particles as a function of pH. Figure 10 is a plot of the saturation magnetization obtained for both microemulsion-derived and co-precipitation barium ferrite particles as a function of pH.
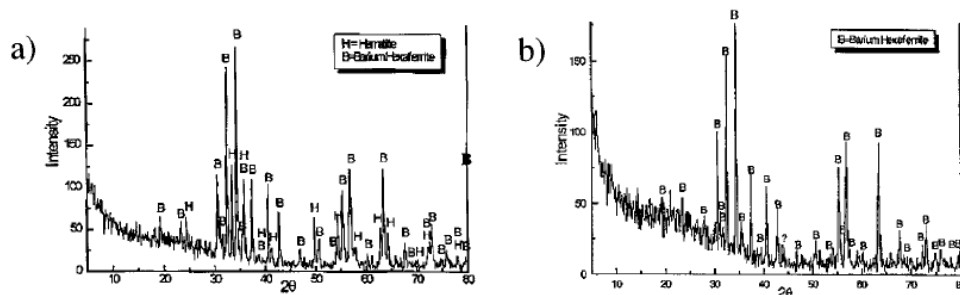

Figure 6. XRD patterns for calcined barium ferrite nanoparticles produced at (a) pH 5, and (b) pH 10.
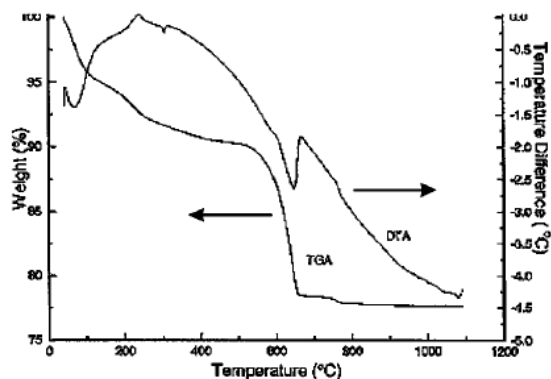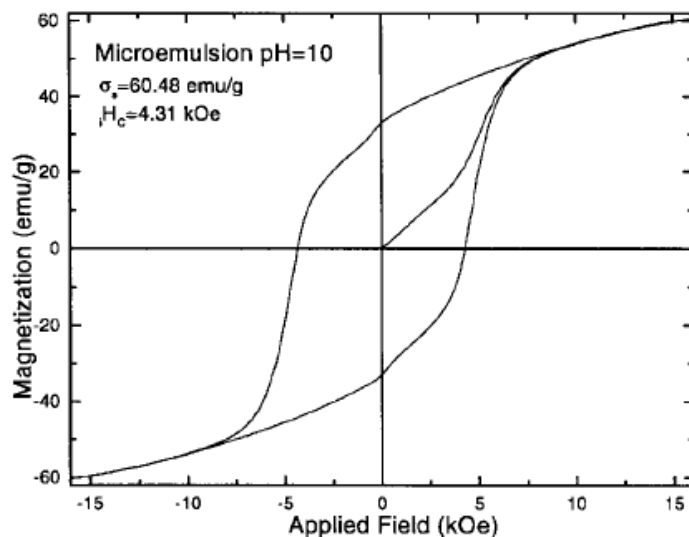

Figure 7. DTA and TGA analysis for precursor particles produced at pH 10.

Figure 8. VSM data for calcined barium ferrite produced from microemulsion at pH 10.

Figure 9 suggests that the intrinsic coercivity is significantly higher for the microemulsion-derived nanoparticles than the co-precipitation particles. The coercivity of the microemulsion-derived nanoparticles is generally >4000 Oe while the coercivity of the co-precipitation particles is <3000 Oe. Figure 10 suggests that the saturation magnetization is also significantly higher for the microemulsion-derived nanoparticles than the co-precipitation particles. The saturation magnetization shows a maximum value of >60 emu/g for pH 10 microemulsion particles. The maximum value for the co-precipitation particles is <50 emu/g. Figures 9 and 10 verify that the particles produced from microemulsion show better magnetic properties than the particles produced by conventional co-precipitation, as expected from the differences in particle size distribution illustrated in Figure 2. The more uniform, smaller size particles with lower defects produced by microemulsion synthesis yield higher coercivity and saturation magnetization values.
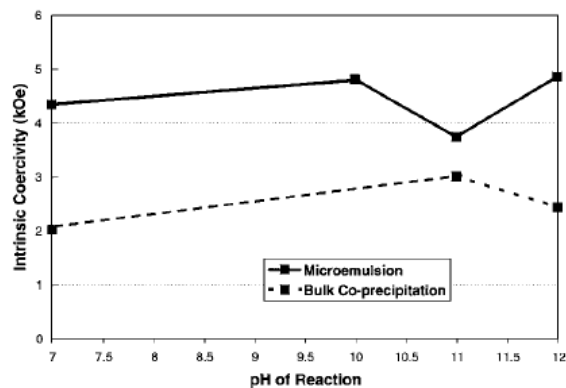
Figure 9. Intrinsic coercivity (H_c) as a function of pH for barium ferrite particles from two different precipitation methods.
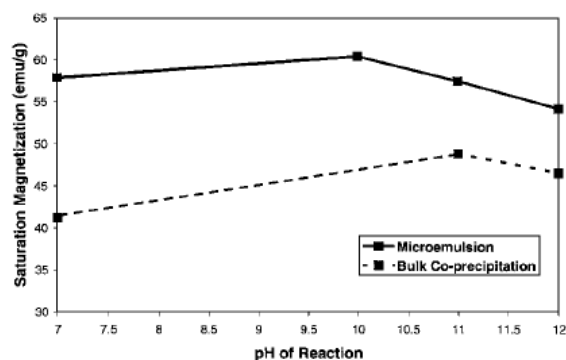

Figure 10. Saturation magnetization (σ_s) as a function of pH for barium ferrite particles from two different precipitation methods.

Conclusions

Microemulsion processing has been investigated as a feasible means of obtaining monodisperse particles of barium ferrite ($BaFe_{12}O_{19}$) in the nanoparticle regime (<0:1 µm). In the microemulsion reaction, ferric nitrate ($Fe(NO_3)_3$) and barium nitrate ($Ba(NO_3)_2$) are reacted with precipitating agents sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3) to form hydroxide and carbonate precursor particles in the correct molar ratio of Fe^{3+} : Ba^{2+}. Calcination of the precursor particles leads to conversion to the hexagonal ferrite phase. For comparison, the particles have also been made by bulk co-precipitation in aqueous solution. By varying the relative

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concentrations of the reactants, the pH of reaction has been investigated as a contributing factor.

TEM images of the precursor particles obtained from microemulsion show spherical nanoparticles with a mean diameter near 10 nm, while the calcined ferrite particles are agglomerated but still smaller than 0.1 μm. XRD of the calcined barium ferrite verifies the presence of the hexagonal ferrite for high pH of reaction. Low pH of reaction results in the presence of some non-magnetic hematite phase. VSM magnetic property measurements reveal excellent properties for the particles derived from microemulsion while the particles made by conventional bulk co-precipitation show a lowered intrinsic coercivity (H_c) and saturation magnetization ($\square$s). By using microemulsion processing, barium ferrite particles were produced with intrinsic coercivity >4000 Oe and saturation magnetization >60 emu/g.

Acknowledgement

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