

Evolution of the Microstructure and Its Influence on the Magnetic Properties of Aerosol Synthesized BaFe₁₂O₁₉ Particles*

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Small BaFe₁₂O₁₉ particles have been synthesized from an aqueous solution of barium and iron nitrates by an aerosol synthesis technique. Starting hollow spherical particles were annealed under several conditions. Hexagonal-like platelets were obtained at the final stage of a sintering process which has been followed by X-ray diffraction and scanning electron microscopy. The influence of the microstructure evolution on the magnetic properties is discussed. © 1992 Academic Press, Inc.

Introduction

Hexagonal ferrites of which the prototype is BaFe₁₂O₁₉ (barium ferrite) are well known not only as permanent magnets, but also as emerging magnetic recording media and as potential magneto-optical devices. The magnetic properties are strongly dependent on preparation method. So considerable efforts have been devoted to preparing pure and doped BaFe₁₂O₁₉ fine particles, smaller than 1 μm, to be used as magnetic recording media. Various techniques have been developed for this purpose; these include the

chemical coprecipitation method (1), the glass crystallization method (2, 3), the so-called liquid mix technique (4, 5), and some colloidal methods (6, 7). More recently, the aerosol synthesis technique has been used to produce small particles of both iron oxides (8) and barium ferrite (9, 10). Its main advantage is that this technique has the potential to create particles of unique composition and magnetic behavior for which the starting materials are mixed in a solution at the atomic level. An ulterior thermal treatment can originate important modifications on morphology and texture.

We describe, in this paper, the synthesis of BaFe₁₂O₁₉ small particles by pyrolysis of an aerosol and the influence of the evolution of its microstructure after thermal treat-

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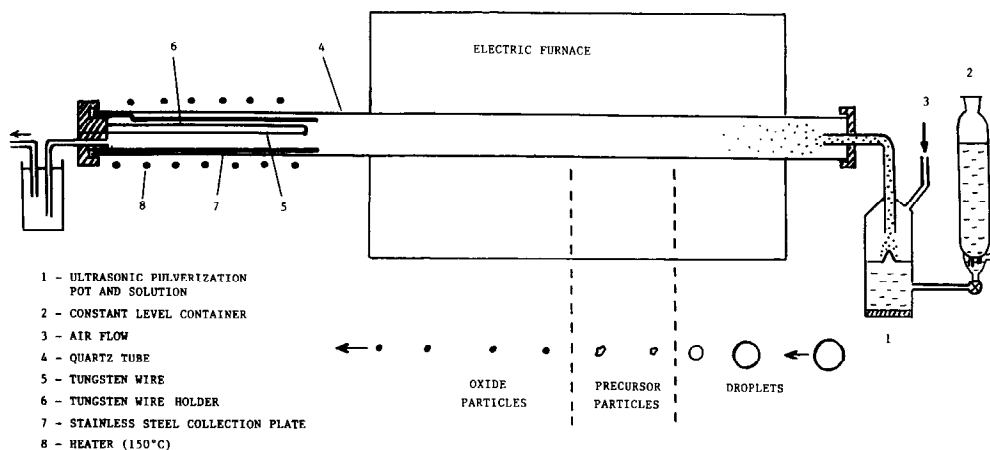


FIG. 1. Schematic representation of the preparation apparatus.

ment, as deduced by X-ray diffraction and scanning electron microscopy, on the magnetic properties.

Experimental

$\text{BaFe}_{12}\text{O}_{19}$ fine particles were synthesized by using pyrolysis of an aerosol generated by ultra high frequency spraying of a solution. The processing equipment is shown in Fig. 1. The aerosol generation system is the same as the one used for thin film deposition of several oxides (11, 12). An ultrasonic transducer is located at the bottom of a vessel which contains a precursor solution of the final material. An ultrasonic beam (850 kHz) is focused close to the surface of this solution. Ultrafine droplets (2–4 μm) are produced above the surface, and this aerosol is conveyed by purified air with a flow rate of 6.5 liters/min.

When thin films are produced, the aerosol is conveyed close to the heated substrate, where precursors are transformed into vapor before pyrolysis and film deposition (conditions of chemical vapor deposition). In the process described here, precursors are not volatile. Consequently, they are not transformed into vapor. The aerosol flow

passes through a 65-cm-long tubular furnace at temperatures between 300 and 900°C. Under these conditions, the residence time of the particles is about 2 sec in the high temperature zone. Thus, the solvent evaporates, leading to the formation of metal precursor particles and, then, submicronic oxide particles (Fig. 1).

Oxide particles are collected outside the furnace with an electrostatic filter. This system does not disturb the gas flow, contrarily to a porous membrane filter. A thin tungsten wire is suspended in the center of a tubular stainless steel collection plate. This wire is charged negatively with 8 kV. Then, the oxide particles are charged and collected on the plate which is kept at 150°C to avoid condensation of water steam. The collection efficiency is about 70–80%. The tungsten wire geometry avoids a powder accumulation on the fixing of the wire and a short circuit of high voltage.

$\text{BaFe}_{12}\text{O}_{19}$ fine particles were obtained at 900°C using this apparatus. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Ba}(\text{NO}_3)_2$ were dissolved in distilled water to 0.03 M concentration, according to the stoichiometry 12:1.

The *in situ* product so obtained (sample A) was the object of several thermal treatments

TABLE I
THERMAL TREATMENT CONDITIONS
AND SAMPLES OBTAINED

Sample	T (°C)	t (hr)	Phases obtained as deduced by XRD
A	900	—	Noncrystalline phase + α -Fe ₂ O ₃
B	900	1	BaFe ₁₂ O ₁₉
C	900	24	BaFe ₁₂ O ₁₉
D	1000	1	BaFe ₁₂ O ₁₉
E	1000	24	BaFe ₁₂ O ₁₉
F	1100	1	BaFe ₁₂ O ₁₉
G	1100	24	BaFe ₁₂ O ₁₉
H	1200	24	BaFe ₁₂ O ₁₉

(see Table I) in order to study the evolution of the microstructure and its influence on the magnetic properties.

Samples were characterized by X-ray diffraction (XRD) on a Siemens D-5000 diffractometer (CuK α radiation). Particle size and shape were analyzed by scanning electron microscopy (SEM) on a JEOL 6400 microscope. Chemical analysis was carried out by energy dispersive spectroscopy (EDS) on a LINK AN 10000 system and by inductive coupling plasma. A vibrating sample magnetometer was used to measure the magnetic properties at room temperature and a maximum field of 8 T.

Results and Discussion

Powder XRD data of sample A can be interpreted as due to the mixture of a majority noncrystalline phase and a small amount of α -Fe₂O₃ (Fig. 2a). Although the treatment temperature is high enough (900°C), the precursor is only at such a temperature for 2 sec, which is too short a time to allow the crystallization of the M phase. However, after 1 hr at 900°C (sample B) broad reflections characteristic of small crystallites of the M phase are observed by XRD (Fig. 2b). Finally, well-crystallized BaFe₁₂O₁₉ is

obtained at 1200°C (sample H) (Fig. 2c). All samples obtained (Table I) were analyzed by SEM for better understanding of the microstructural evolution as a function of the thermal treatment.

Figure 3a shows a scanning electron micrograph of the starting material (sample A), mainly formed by hollow spherical particles of a diameter ranging between 0.12 and 1.3 μ m and a thickness of around 0.1 μ m. EDS analysis indicates that the constituent cations of these particles are Ba and Fe. Quantitative chemical analysis performed by ICP shows an average cationic ratio 1 : 12.

When the treatment time is increased, the particles keep the original spherical shape. However, SEM micrographs clearly show they are not constituted by smaller particles (Figs. 3b and 3c). Such small particles will

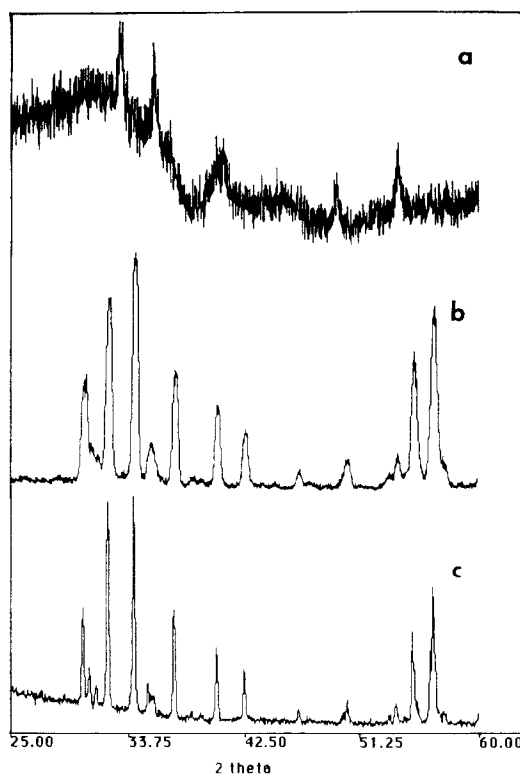


FIG. 2. Powder XRD of (a) sample A; (b) sample B; and (c) sample H.

be referred in the following as crystallites. The crystallite average size, as deduced from the width of XRD maxima by applying the classical Scherrer equation, varies from 30 to 40 nm for sample B and from 50 to 80 nm for sample C.

Crystallites constituting spherical particles grow up as the temperature is increased up to 1000°C (samples D and E). Elongated crystallites ($\approx 0.1 \times 0.3 \mu\text{m}$) can be seen on the grain surface, leading to a small deviation of the spherical shape (Figs. 3d and 3e). It can also be observed that a sintering process starts at this temperature. X-ray diffraction shows that the formation process has been completed at this temperature. This process is accelerated when the temperature reaches 1100°C, although two stages can be clearly distinguished as a function of the treatment time.

(a) After 1 hr at 1100°C (sample F) the powder seems to be formed, as seen in Fig. 3f, by a mixture of particles showing different morphologies. Spherical particles constituted by small crystallites are now mixed with plateletlike particles probably formed as a consequence of the sintering process started at 1000°C by linkage between elongated crystallites. The particle average size, as deduced from SEM, varies between 0.6 and 1.5 μm .

(b) After 24 hr (sample G) the spherical shape disappears. Only plateletlike particles showing heterogeneous shape and size (1–3 μm) are observed (Fig. 3g).

Finally, a considerable increasing of the particle size is observed when the temperature reaches 1200°C. The initial particles, having agglomerated, appear now as well-formed hexagonal platelets with an average diameter ranging between 2 and 6 μm (Fig. 3h).

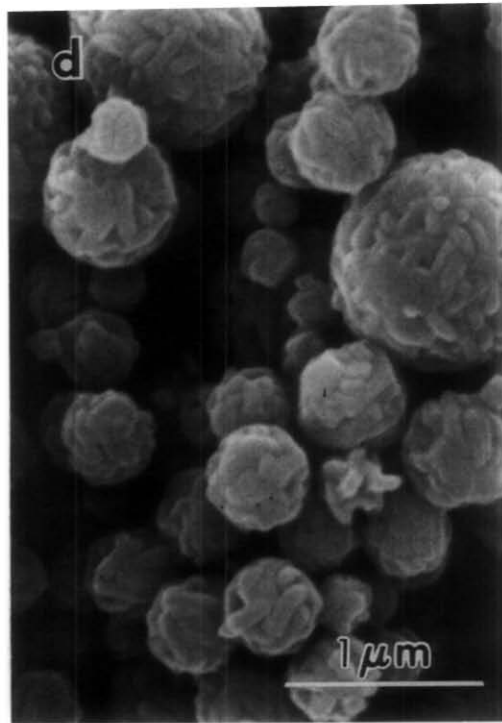
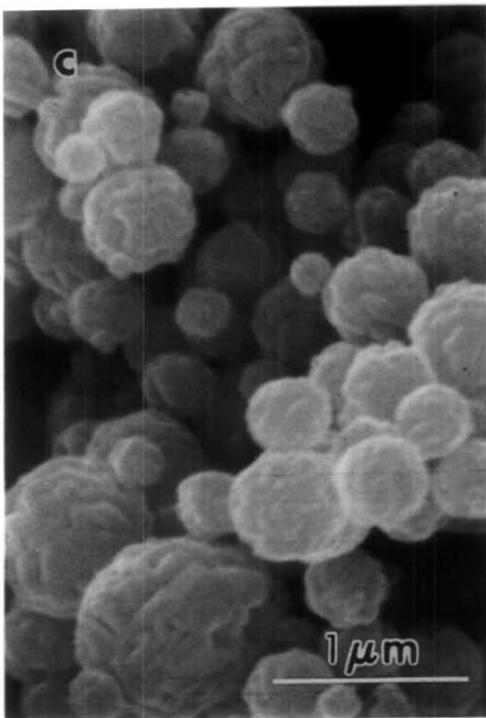
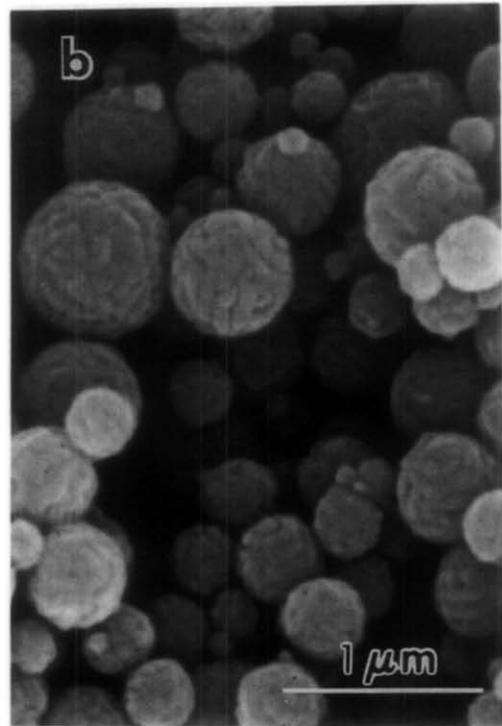
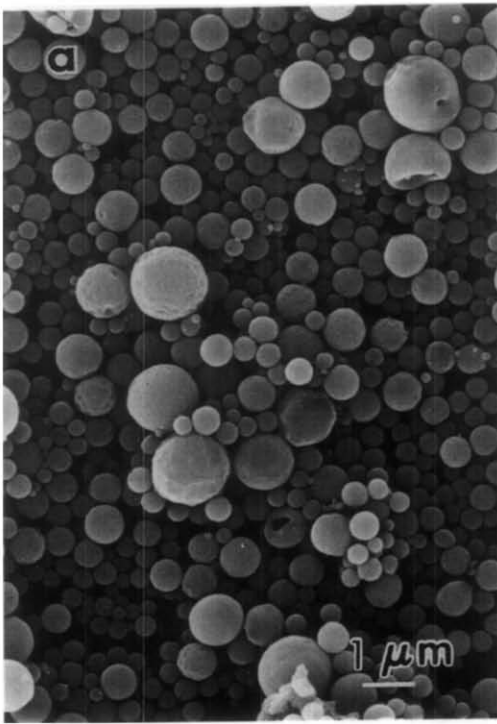
The crystallization process has also been followed by means of an electron diffraction study which confirms the results obtained by XRD. Thus, spherical particles of sample A do not show any reflection which could be either due to nonperiodic order or as a consequence of the sphere thickness. However, when the crystallites appear along the annealing treatment, electron diffraction patterns characteristic of a polycrystalline M phase are recorded. Finally, hexagonal plateletlike particles give diffraction patterns corresponding to those of the M phase.

In order to summarize the evolution of the microstructure as a function of the thermal treatment, the most significant morphological parameters are listed in Table II. From the ensemble of these results, the sintering process depicted in Fig. 4 can be proposed.

This evolution is obviously reflected in the magnetic properties of $\text{BaFe}_{12}\text{O}_{19}$ as can be deduced from saturation magnetization (M_s), remanent magnetization (M_r), and coercive field (H_c) values, which are listed in Table II. The initial magnetization curve of all samples and their corresponding enlargement (Fig. 5) clearly show the variation of the magnetization process as a function of both the particle shape and the particle size.

The as-received sample shows low magnetization at 8 T (5.8 emu/g). Both the first magnetization curve (Fig. 6) and the hysteresis loop (Fig. 7) seem to be characteristic of a superparamagnetic material. However, some anomalies are observed (note that Fig. 6 is an enlargement of curve A in Fig. 5) in both curves which indicate the presence of two phases. This low magnetization value is characteristic of a weakly magnetic material. However, both X-ray and electron diffraction do not allow us to characterize with

FIG. 3. Scanning electron micrographs of (a) sample A; (b) sample B; (c) sample C; (d) sample D; (e) Sample E; (f) sample F; and (h) sample H.



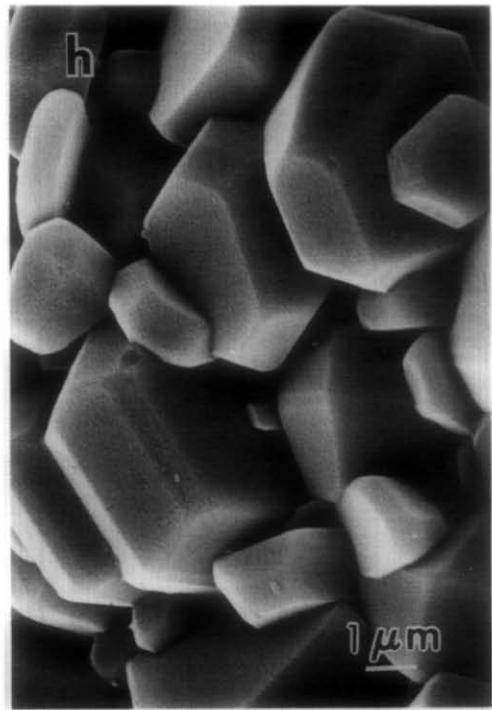
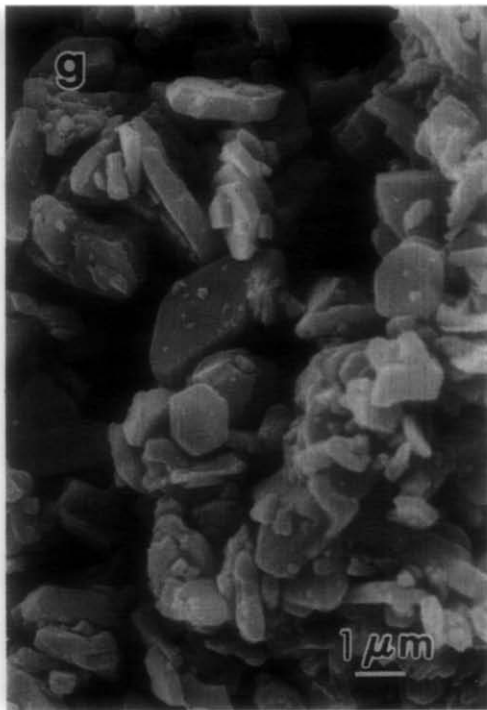
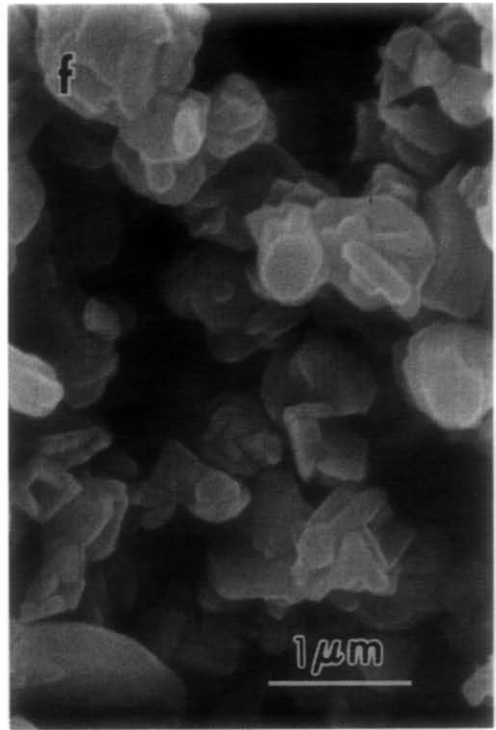
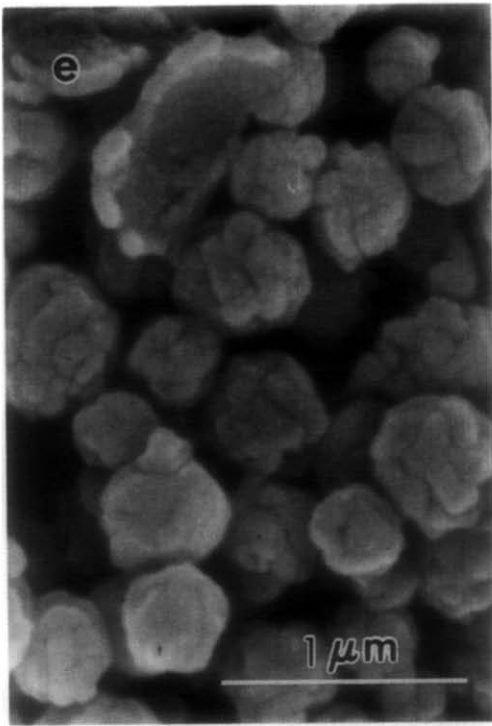


FIG. 3-Continued

TABLE II
SHAPE PARTICLE, CRYSTALLITE SIZE, AND HYSTERESIS PROPERTIES OF ALL SAMPLES OBTAINED

Sample	Shape particle (size, μm)	Crystallite size (nm) (XRD)	Sintering ^a	M_s (emu/g)	M_r (emu/g)	M_r/M_s	H_c (Oe)
A	Spherical (1.3–0.12)	—	No	5.8	0.39	0.07	1325
B	Spherical (1.3–0.12)	30–40	No	70.7	34.5	0.49	4867
C	Spherical (1.3–0.12)	50–80	No	75.5	36.5	0.48	4730
D	Spherical ^b (1.3–0.12)	80–120	Yes	69.1	33.9	0.49	4815
E	Spherical ^b (1.3–0.12)	300 \times 100 ^c	Yes	69.2	34.1	0.49	4535
F	Spherical + platelet (0.6–1.5)	—	Yes	76.2	36.6	0.48	3725
G	Platelet (1–3)	—	Yes	77.8	36.7	0.47	2390
H	Hexagonal platelet (2–6)	—	No	76.7	32.3	0.42	1500

^a The sintering mechanisms can be evaluated from SEM. The agglomeration process starts at 1000°C (sample D). In sample H the sintering process has already finished.

^b Small deviations of the spherical shape can be appreciated.

^c When the average crystallite size is higher than ≈ 200 nm the Scherrer equation cannot be applied. Dimensions are then determined from scanning electron micrographs.

more detail the nature of sample A, whose H_c value is ≈ 1325 Oe.

The first magnetization curve of samples treated at $T \leq 1000^\circ\text{C}$ is characteristic of single domain particles. From B to C samples, M_s increases as the crystallite size increases (Table II). However, sample D shows a much lower magnetization value as a consequence of the beginning of the

sintering process between crystallites since the material is perturbed in the grain links. The squareness ratio (M_r/M_s) is very close to 0.5, i.e., to the theoretical value of single domain particles having uniaxial anisotropy. On the contrary, G and H samples have higher M_s values, their first magnetization curves being characteristic of polydomain particles.

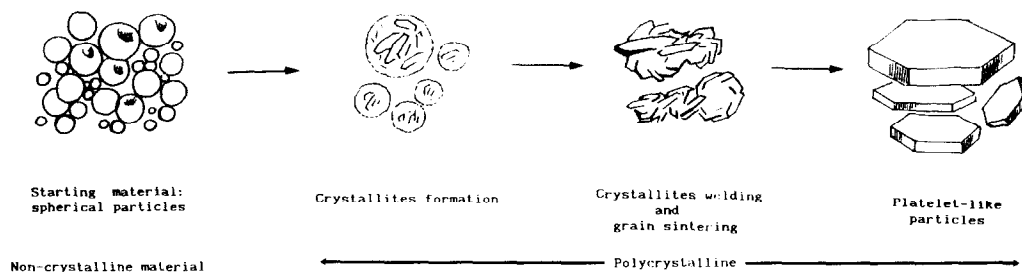


FIG. 4. Tentative diagram of the microstructure evolution of BaFe₁₂O₁₉ fine particles.

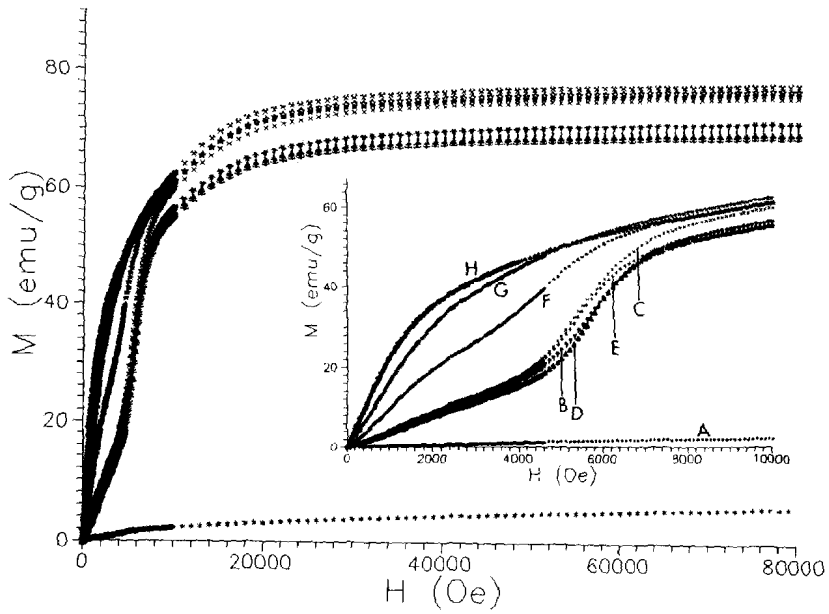


FIG. 5. Initial magnetization curves of all the samples at 8 T. An enlargement is shown at the onset.

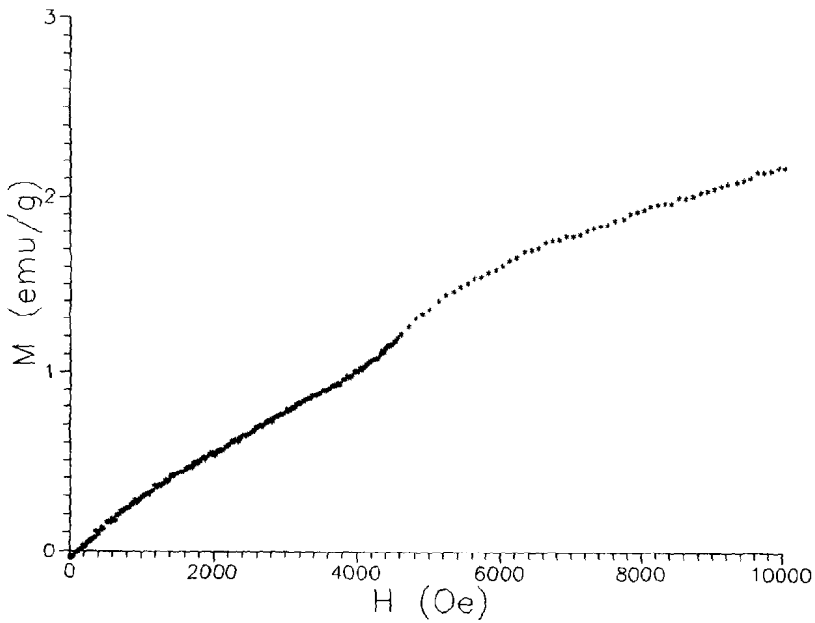


FIG. 6. Enlargement of the initial magnetization curve corresponding to sample A.

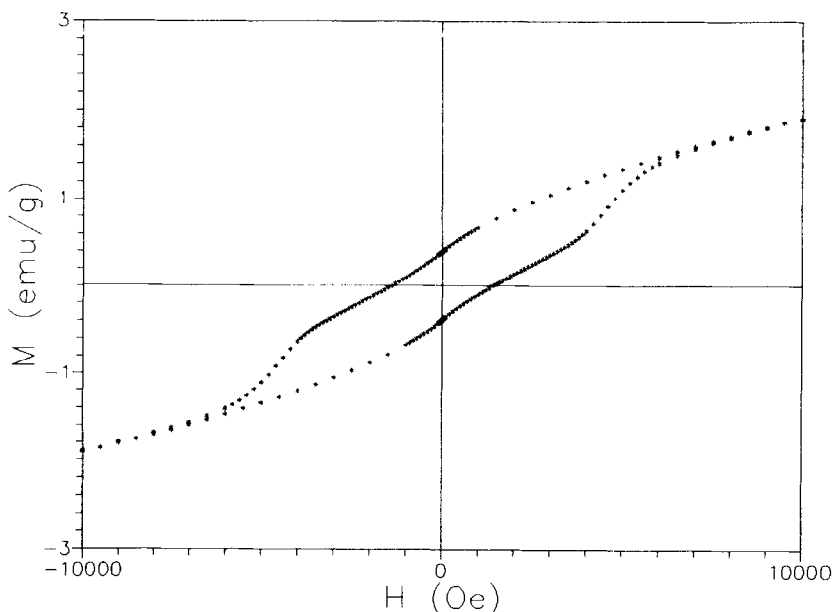


FIG. 7. Hysteresis loop corresponding to sample A.

The magnetic properties of sample F clearly emphasize this remarkable evolution since two magnetization processes are involved due to grain dispersions. Moreover, from F to H samples dramatic changes are observed. Thus, the highest value of the coercive field (4867 Oe), observed in single domain particles of 30–40 nm (sample B), decreases to 1500 Oe for well-crystallized hexagonal platelets (2–6 μm), whose t/D ratio (t , thickness; D , diameter) decreases from F to H. The H_c evolution in the final stage of the sintering process is due to the appearance of an important demagnetized field in the platelet planes, but also to more complex magnetic mechanisms due to the presence of polydomain particles.

Conclusions

The synthesis of BaFe₁₂O₁₉ by means of pyrolysis of an aerosol leads to small hollow spherical particles. The ulterior thermal

treatment modifies both the shape and the size of crystallites. The initial spherical shape is destroyed at high temperature.

Magnetic properties are strongly dependent on the texture of crystallites. A single domain particle behavior with uniaxial anisotropy is observed for an average particle size lower than 0.1–0.2 μm , but a monodomain–polydomain behavior for higher values. Small secondary effects on the magnetization are also observed when the sintering process starts.

Acknowledgments

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