

# Co-Ti Substituted Hexagonal Ferrites for Magnetic Recording

M. V. Cabañas,\* J. M. González-Calbet,†‡ and M. Vallet-Regí\*·‡<sup>1</sup>

\*Departamento Química Inorgánica y Bioinorgánica, Facultad de Farmacia, Universidad Complutense, 28040 Madrid, Spain; †Departamento Química Inorgánica, Facultad de Químicas, Universidad Complutense, 28040 Madrid, Spain; and ‡Instituto de Magnetismo Aplicado, Apdo. 155, Las Rozas, 28230 Madrid, Spain

Received January 10, 1994; in revised form August 2, 1994; accepted August 11, 1994

BaFe<sub>12-2x</sub>Co<sub>x</sub>Ti<sub>x</sub>O<sub>19</sub> (0 < x < 1) samples have been synthesized by four different preparation methods: the so-called liquid mix technique, chemical coprecipitation, pyrosol method, and hydrothermal synthesis. The optimum conditions for obtaining single phases with a particle size smaller than 1 μm have been investigated. As a consequence of both the synthetic procedure and the particle size, samples with coercivity varying from 5500 to 255 Oe have been obtained. © 1995 Academic Press, Inc.

## INTRODUCTION

Magnetic recording media using barium hexaferrite particles have been shown to be promising media for high density magnetic recording (1-3). However, the intrinsically large coercivity of pure BaFe<sub>12</sub>O<sub>19</sub> single domain particles convenient for the manufacturing of permanent magnets can be reduced to values suitable for magnetic recording applications. The substitution of iron ions by cobalt and titanium is a commonly used method to reduce the strong anisotropy of BaFe<sub>12</sub>O<sub>19</sub> and, therefore, to make these particles suitable for such a purpose (4-6). Moreover, the magnetic properties are strongly dependent on the preparation method. In this sense, several synthetic routes have been proposed to obtain samples with a particle size smaller than 1 μm (7-9).

We describe in this paper the synthesis of BaFe<sub>12-2x</sub>Co<sub>x</sub>Ti<sub>x</sub>O<sub>19</sub> (0 < x < 1) samples by four different preparation methods. The morphological, structural, and magnetic properties of samples so obtained are discussed.

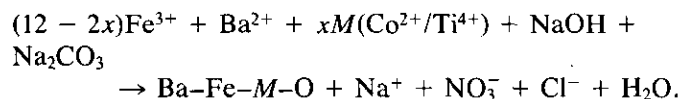
## EXPERIMENTAL

BaFe<sub>12-2x</sub>Co<sub>x</sub>Ti<sub>x</sub>O<sub>19</sub> hexaferrites with 0 < x < 1 were prepared by different synthesis routes. In all cases the synthesis temperature was lower than 900°C.

1. *Liquid mix technique.* This procedure is based on the formation of metallic complexes from concentrated

solutions of polyfunctional organic acids and either salts or oxides of suitable cations for mixed oxide formation (10-12). We have prepared a citric acid solution containing the metallic ions in a stoichiometric proportion for different x values. The Fe ions were introduced as an amorphous precipitate previously obtained by dissolving nitrates in distilled water, precipitating with an ammonium solution, and washing with water until neutrality. Then, a stoichiometric mixture of this precipitate with BaCO<sub>3</sub>, Co(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O, and [(CH<sub>3</sub>)<sub>2</sub>CHO]<sub>4</sub>Ti (0 ≤ x ≤ 0.9), was dissolved in the citric acid solution. Then, ethylene glycol was added to obtain a resin, avoiding the formation of partial segregations which could modify the homogeneity of the solution. To eliminate the organic resin, the samples were heated at 450°C. Finally, the samples were heated in air according to the thermal treatment: 600°C (70 hr) → 700°C (3 hr) → 800°C (2 hr) → 900°C (1 hr) (samples LMT).

2. *Chemical coprecipitation.* The desired stoichiometric amounts of Ba(NO<sub>3</sub>)<sub>2</sub>, Fe(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O, Co(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O, and TiCl<sub>4</sub> were dissolved in distilled water. This solution is added to a Na<sub>2</sub>CO<sub>3</sub>/NaOH (pH 13) solution with vigorous stirring at 60°C for 1 hr. The precipitate formed was cooled at room temperature. The chemical reaction may be described as



Then, after coprecipitation, the soluble salt will remain in the slurry. According to Zheng *et al.* (13), it seems that the presence of Na<sup>+</sup> facilitates the barium ferrite formation. In this sense, we have prepared two series of materials which differ in the washing procedure: samples CCA, which were washed down to pH 7, and samples CCB, washed down to pH 11. Then, both series of samples were subjected to the same thermal treatment as samples LMT.

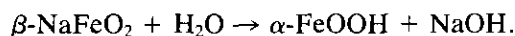
3. *Pyrosol method.* In a previous paper (14), BaFe<sub>12</sub>O<sub>19</sub>

<sup>1</sup> To whom correspondence should be addressed.

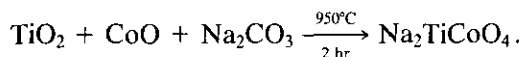
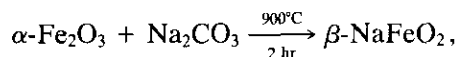
particles were synthesized by pyrolysis of an aerosol generated by ultrahigh frequency of a solution. The same method was used for obtaining  $\text{BaFe}_{10.2}\text{Co}_{0.9}\text{Ti}_{0.9}\text{O}_{19}$  particles; the precursor utilized to produce the aerosol was a citrate solution obtained as previously described for samples LMT. The pyrolysis temperature was  $450^\circ\text{C}$  (sample PM).

4. *Hydrothermal method.* Considering the different factors that influence the hydrothermal synthesis we have developed this method by using two different precursors and modifying temperature, reaction time, and pH.

Precursor 1 was an aqueous suspension of  $\beta\text{-NaFeO}_2$ ,  $\text{Na}_2\text{TiCoO}_4$ , and  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  (Samples HM $\beta$ ). Sodium ferrites were first used in the hydrothermal method by Gaud and Jourbet (15) for the synthesis of  $\text{BaFe}_{12}\text{O}_{19}$ . The advantage of this procedure is that NaOH addition is not necessary, as a consequence of the reaction involved (16):



Then, the metal precursors necessary to obtain barium-doped ferrite, were synthesized by solid state reaction according to the reactions



Since  $\alpha\text{-Fe}_2\text{O}_3$  and/or  $\text{BaTiO}_3$  appear easily, several experiments were done with a different cationic ratio in order to obtain a single substituted barium ferrite:  $\text{Ba}/\text{Fe} = 1/4$  and  $\text{Co}, \text{Ti}/\text{Fe} = 1/8$ ;  $\text{Ba}/\text{Fe} = 1/6$  and  $\text{Co}, \text{Ti}/\text{Fe} = 1/12$ ;  $\text{Ba}/\text{Fe} = 1/8$  and  $\text{Co}, \text{Ti}/\text{Fe} = 1/16$ .

Precursor 2 was an aqueous suspension of the Ba-Fe-Co-Ti-O coprecipitate previously described in the chemical coprecipitation method for  $x = 0.5$  (samples HMC). In this case, the cationic ratio was fixed according to the stoichiometric amounts.

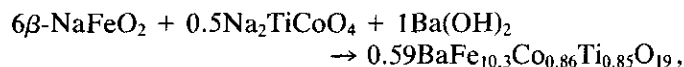
Then, an aqueous suspension of either precursor 1 or 2 was introduced into a gold flask. The experiments were performed in an autoclave which was heated at a rate of 3 to  $4^\circ\text{C}/\text{min}$ , kept at temperatures between  $300\text{--}500^\circ\text{C}$  for different times (17 to 48 hr), and finally, cooled to room temperature. The resulting samples were washed with water, then treated several times with acetone, and finally, dried in air.

All samples were characterized by X-ray diffraction (XRD) on a Siemens D-5000 diffractometer ( $\text{CuK}\alpha$  radiation). Chemical analysis was carried out by inductive coupling plasma (ICP) on a JY70 PLUS and flame spec-

troscopy on a Perkin-Elmer 2380. Carbon elemental analysis was performed on a Perkin-Elmer 2400 CHN analyzer. Particle size and morphology were analyzed by scanning electron microscopy (SEM) on a JEOL 6400 electron microscope. Magnetic measurements were carried out at room temperature in a magnetic field up to 8 T, using a vibrating sample magnetometer (VSM 3001).

## RESULTS AND DISCUSSION

Quantitative chemical analysis performed by ICP shows that the cationic composition of the starting solution is maintained in samples LMT, CCA, CCB, and PM. In samples obtained by the hydrothermal method, the starting cationic ratio ( $1\text{Ba}:11\text{Fe}:0.5\text{Co}:0.5\text{Ti}$ ) is only kept when Ba-Fe-Co-Ti-O coprecipitate is used, but  $\text{Ba}^{2+}$  deficiency with respect to the starting product is observed when sodium ferrite is utilized as precursor. Thus, in samples synthesized according to the reaction



the quantitative analysis indicates that only 60% of the  $\text{Ba}^{2+}$  ions are soluble and form the barium ferrite, while the other cations keep the starting ratio. This justifies the use of  $\text{Ba}^{2+}$  excess in the barium hexaferrite synthesis.

The analysis by flame spectroscopy indicates the presence of about 1% sodium in samples CCB. No sodium was detected in products obtained by hydrothermal synthesis.

An elemental analysis was performed in samples synthesized from an organic precursor. The results obtained only show the presence of organic matter in the product obtained by the pyrosol method: 12.6% C and 1.4% H.

The evolution of the starting products with the thermal treatment has been followed by XRD. When the liquid mix technique is used, single phase materials showing the magnetoplumbite-like structure are obtained for  $x \leq 0.5$ . Since the synthesis temperature is relatively low ( $900^\circ\text{C}$ ), in samples with higher  $x$  values, a small amount of  $\alpha\text{-Fe}_2\text{O}_3$  is also observed. In products obtained from chemical coprecipitation, a different evolution in both CCA and CCB series as a function of the thermal treatment was observed (Fig. 1). In samples CCA, the barium ferrite crystallizes at temperatures around  $800^\circ\text{C}$  although this phase is accompanied by a small amount of  $\alpha\text{-Fe}_2\text{O}_3$  at  $900^\circ\text{C}$ . The presence of  $\text{Na}^+$  ions in samples CCB favors barium ferrite formation which is already formed at  $600^\circ\text{C}$ , although a single  $M$  phase is obtained only from  $800^\circ\text{C}$  for all  $x$  values.

As a consequence of the short residence time of the particles in the high temperature zone (about 2 sec), an amorphous material was obtained by the pyrosol method.

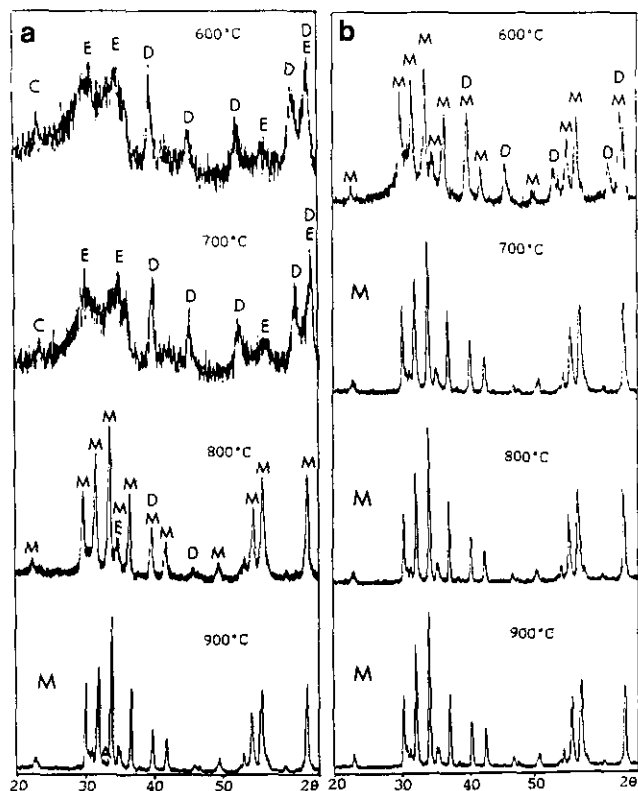


FIG. 1. Powder XRD patterns of samples (a) CCA and (b) CCB as a function of the thermal treatment ( $x = 0.9$ ) (A,  $\alpha$ - $\text{Fe}_2\text{O}_3$ ; C,  $\text{BaCO}_3$ ; E, spinel; D,  $\epsilon$ -(Fe, Co, Ti) $_2\text{O}_3$ ; M, barium hexaferrite).

(sample PM). The same phenomenon was observed in the synthesis of pure  $\text{BaFe}_{12}\text{O}_{19}$  (17). The magnetoplumbite-like structure was obtained by an ulterior treatment at  $900^\circ\text{C}$  for 1 hr (sample PMT).

On the other hand, in the hydrothermal synthesis, the experiments performed with precursor 1 show that a  $\text{Ba}(\text{OH})_2$  excess is necessary in order to avoid  $\alpha$ - $\text{Fe}_2\text{O}_3$  formation. However, there exists a threshold in the  $\text{Ba}^{2+}$  excess from which the  $\text{BaTiO}_3$  formation is favored. Under the same temperature and reaction time conditions, the best results (barium hexaferrite as the majority phase) were obtained when the cationic ratio  $\text{Ba}/\text{Fe} = 1/6$  was used. In the same way, although  $\text{NaOH}$  is released in the precursor hydrolysis, barium ferrite formation is more favorable when the suspension pH is increased. A similar effect is observed when both temperature and time increase. It should be emphasized that by this method, the temperature needed to obtain the Co-Ti substituted barium hexaferrite is significantly lower than in the other methods, probably due to the bigger pressure used. Then, a single phase is obtained at  $400^\circ\text{C}$  for 48 hr for a cationic ratio  $\text{Ba}/\text{Fe} = 1/6$  (sample HM $\beta$ 1). In the case of precursor 2 (Ba-Fe-Co-Ti-O coprecipitate),  $\text{NaOH}$  addition is necessary to obtain barium ferrite, which appears as a

single phase at  $400^\circ\text{C}$  for 17 hr (sample HMC1). In general, the results obtained by hydrothermal synthesis using different conditions show a higher reactivity when precursor 2 is used.

In order to follow the evolution of both the morphology and the particle size, a SEM study was performed. Figures 2–5 show the SEM micrographs of samples obtained by the different methods. These photographs allow one to observe the variety of particle shapes and sizes of Co-Ti substituted barium hexaferrite as a function of the preparation method.

The samples obtained by the liquid mix technique and chemical coprecipitation are formed by small particles. The SEM photographs show a homogeneous size distribution:  $0.05$ – $0.1 \mu\text{m}$  in samples LMT (Fig. 2),  $0.09$ – $0.13 \mu\text{m}$  in samples CCA (Fig. 3a); and  $0.17$ – $0.22 \mu\text{m}$  in samples CCB (Fig. 3b). The same average size was observed for all  $x$  values. It is worth mentioning that in liquid mix technique synthesized samples  $\text{BaFe}_{12-2x}\text{Co}_x\text{Sn}_x\text{O}_{19}$  ( $0 < x < 1$ ) a progressive increase in the mean crystal size was observed as the  $x$  value increases (18).

When the sample obtained by the pyrosol method was treated at the same temperature as the LMT, CCA, and CCB samples ( $900^\circ\text{C}$  for 1 hr), the Co-Ti substituted barium hexaferrite obtained is formed by a defined particle morphology, with small hexagonal platelets ( $0.2$ – $0.4 \mu\text{m}$ ) being observed in the sample PMT (Fig. 4).

On the other hand, a well-defined particle morphology is observed in products obtained by hydrothermal syn-

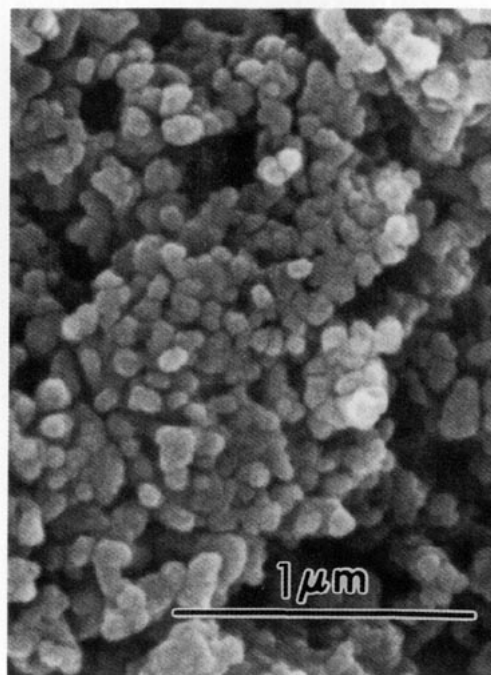


FIG. 2. Scanning electron micrograph of the  $x = 0.5$  LMT sample.

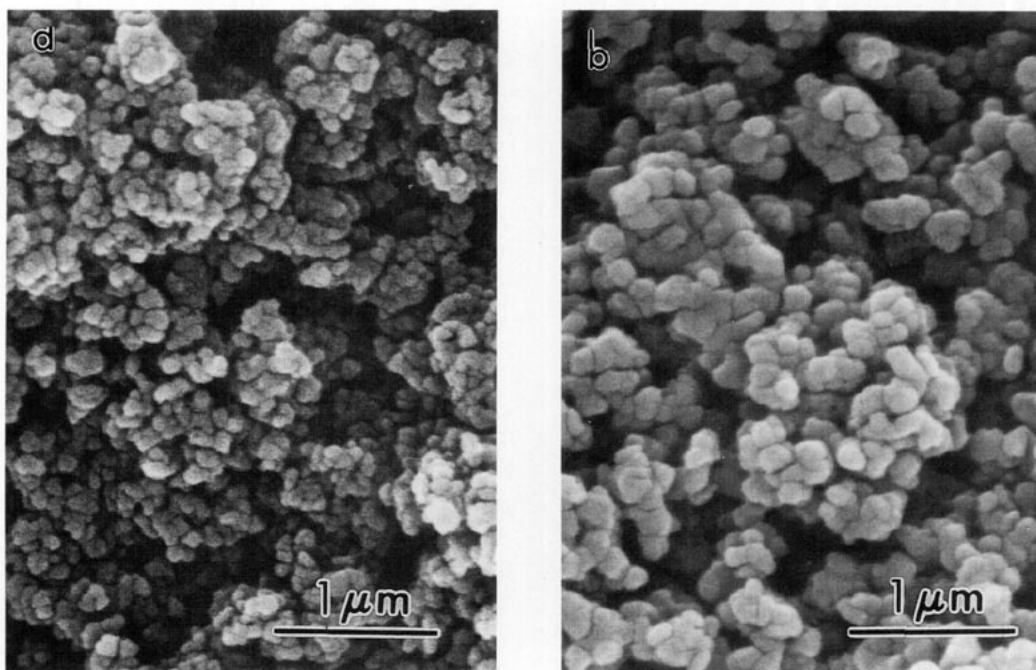


FIG. 3. Scanning electron micrographs of  $x = 0.5$  samples obtained by chemical coprecipitation (a) CCA and (b) CCB.

thesis. Thus, when Ba-Fe-Co-Ti-O coprecipitate is used as the precursor, homogeneous samples composed of hexagonal platelets are observed. In the case of precursor 1, the samples obtained seem to be composed of

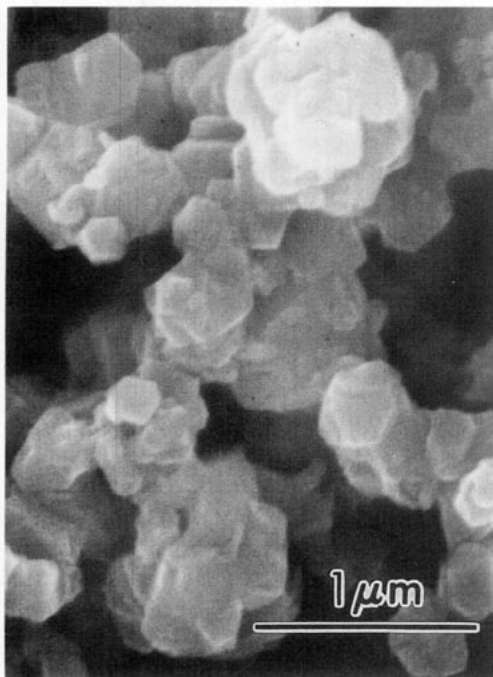


FIG. 4. Scanning electron micrograph of  $x = 0.9$  sample PMT obtained by the pyrosol method.

more heterogeneous particles, probably due to the lower reactivity of this precursor. In both cases, both the particle size and distribution are modified by the reaction conditions. An increase in the reaction time, the temperature, or the suspension pH lead to an increase in both the average size and the homogeneity of the particles. Figure 5a shows a SEM micrograph of HMC1 material, where hexagonal platelets, with an average diameter ranging between 1 and 2  $\mu\text{m}$  and with a thickness of about 0.2  $\mu\text{m}$ , can be observed. Bigger platelets ( $\sim 6 \mu\text{m}$ ) are obtained by using precursor 1, as shown in Fig. 5b (sample HM $\beta$ 1).

The different characteristics observed in samples obtained by the four synthetic methods are reflected in their magnetic properties. Results corresponding to saturation magnetization ( $M_s$ ), remanent magnetization ( $M_r$ ), and coercive field ( $H_c$ ) measured at room temperature are listed in Table I.

The results obtained show that for the preparation methods in which the amount of substitution is easily controllable, such as the liquid mix technique or chemical coprecipitation, the coercivity,  $H_c$ , is also easily controllable within a wide range (5550–1030 Oe) without significant reduction in magnetization,  $M_s$ . Then, in samples LMT, a decrease of about 81% is observed in  $H_c$  values with varying  $x$  from 0 to 0.9. However, for the same  $x$  value the decrease observed in  $M_s$  values is only 12%. The decrease in both magnetic properties is in agreement with the results obtained by other authors in the Ba

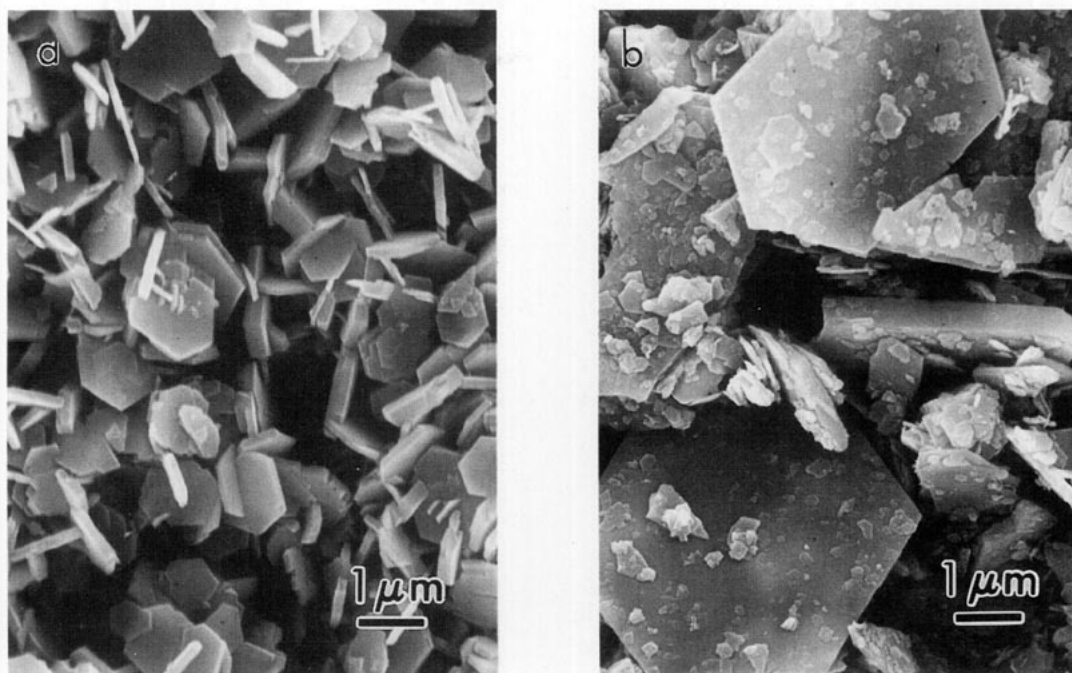


FIG. 5. Scanning electron micrographs of samples obtained by hydrothermal method (a) HMC1 and (b) HMβ1.

$\text{Fe}_{12-2x}\text{Co}_x\text{M}_x\text{O}_{19}$  system ( $M = \text{Ti}^{4+}, \text{Sn}^{4+}$ ). This variation is attributed to the decrease in the magnetic anisotropy by introduction of  $\text{Co}^{2+}$  ions in octahedral positions (19, 20). Then, if this composition dependence of  $H_c$  in Co-Ti substituted ferrites is compared to that observed in Co-Sn particles obtained by the liquid mix technique, it may

be observed that similar values of the coercive field are obtained with a smaller Co-Sn substitution (18). This difference seems to be due to the different cationic distribution in both series. Thus, neutron diffraction studies show that the amount of  $\text{Co}^{2+}$  ions located in octahedral positions is higher when  $M = \text{Sn}^{4+}$  than in the case of  $\text{Ti}^{4+}$  ions (21, 22). Cationic composition can also be accurately controlled by using the pyrosol method. There, the  $H_c$  value can also be adjusted between 4670 Oe for  $x = 0$  (17) and 815 Oe for  $x = 0.9$ .

On the other hand, the contribution of the shape anisotropy must be considered. In this sense, Kubo *et al.* (23) observed that  $H_c$  decreases as the diameter/thickness ratio of platelets increases. This fact could justify the different characteristics observed in samples with the same substitution value ( $x = 0.5$ ) and obtained by different synthesis methods. In Fig. 6, the  $H_c$  variation with particle size, for samples with the same Co-Ti content and obtained by different preparation methods, is observed. This plot shows that the increase in the particle size (or the diameter/thickness ratio) contributes to a decrease in the coercivity.

## CONCLUSIONS

Co-Ti substituted barium ferrites have been synthesized by four different preparation methods: liquid mix technique, chemical coprecipitation, pyrosol method, and hydrothermal synthesis. Samples with different par-

TABLE 1  
Magnetic Properties of  $\text{BaFe}_{12-2x}\text{Co}_x\text{Ti}_x\text{O}_{19}$  ( $0 \leq x \leq 1$ )  
Samples Obtained by Different Synthesis Methods

| Samples | $x$ Value        | $H_c$ (Oe) | $M_s$ (emu/g) | $M_r$ (emu/g) |
|---------|------------------|------------|---------------|---------------|
| LMT     | 0                | 5550       | 74.9          | 36.2          |
|         | 0.3              | 4535       | 72.9          | 34.0          |
|         | 0.5              | 3595       | 70.3          | 33.4          |
|         | 0.6 <sup>a</sup> | 2860       | 70.2          | 33.3          |
|         | 0.7 <sup>a</sup> | 2280       | 68.5          | 32.2          |
|         | 0.9 <sup>a</sup> | 1030       | 66.1          | 28.0          |
| CCA     | 0.3 <sup>a</sup> | 3990       | 73.8          | 34.7          |
|         | 0.5 <sup>a</sup> | 2935       | 72.0          | 33.1          |
|         | 0.9 <sup>a</sup> | 1000       | 66.7          | 25.8          |
| CCB     | 0.3              | 3430       | 70.8          | 33.1          |
|         | 0.5              | 2500       | 68.8          | 31.4          |
|         | 0.9              | 570        | 63.1          | 20.0          |
| PMT     | 0.9              | 815        | 67.0          | 26.6          |
| HMβ1    | 0.85             | 255        | 64.9          | 7.6           |
| HMC1    | 0.5              | 810        | 64.8          | 21.4          |

<sup>a</sup> A small amount of  $\alpha\text{-Fe}_2\text{O}_3$  is also observed.

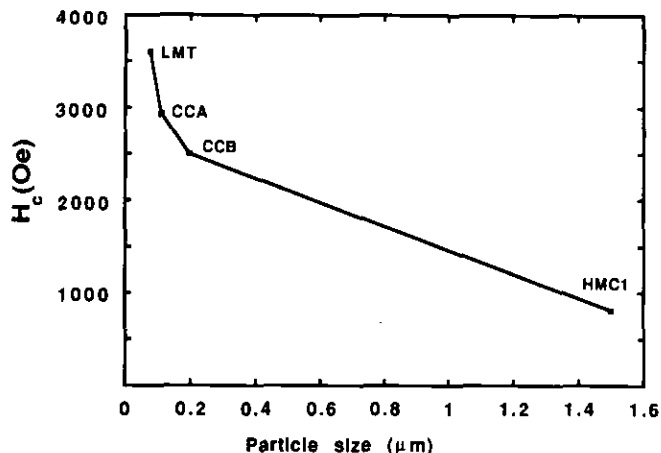


FIG. 6. Coercive field of  $\text{BaFe}_{11}\text{Co}_{0.5}\text{Ti}_{0.5}\text{O}_{19}$  samples obtained by different synthetic methods as a function of the particle size.

ticle size and morphology have been obtained. The results show that the magnetic properties, mainly the coercive field, are dependent on both particle size and Co-Ti content. These factors can be independently controlled to obtain a specific coercivity at a given particle size. The coercivity is controllable in a wide range (5550–255 Oe) and the decrease in magnetization is relatively small, its value being satisfactory for magnetic recording media. In any case, the synthetic method contributes to the control of all these parameters.

#### ACKNOWLEDGMENTS

The authors are grateful to Drs. X. Obradors, M. Pernet, and P. Mollard for helpful discussions on magnetic data. We also thank J. L. Baldonado and D. Boursier for valuable technical assistance. Financial support from the Comision Interministerial de Ciencia y Tecnologia

(CICYT, Spain) through Projects MAT91-0331 and MAT93-0207 is also acknowledged.

#### REFERENCES

1. S. Iwasaki and Y. Nakamura, *IEEE Trans. Magn.* **13**, 1272 (1977).
2. O. Kubo, T. Ido, and H. Yokoyama, *IEEE Trans. Magn.* **18**, 1122 (1982).
3. T. Fujiwara, *IEEE Trans. Magn.* **21**, 1480 (1985).
4. T. Ido, O. Kubo, and H. Yokoyama, *IEEE Trans. Magn.* **22**, 704 (1986).
5. G. Turilli and A. Paoluzi, *IEEE Trans. Magn.* **24**, 2865 (1988).
6. V. V. Pankov, M. Pernet, P. Germi, and P. Mollard, *J. Magn. Magn. Mater.* **120**, 69 (1993).
7. M. Kiyama and T. Takada, *Adv. Ceram.* **15**, 61 (1985).
8. E. Marcello, B. Grange, J. C. Joubert, and P. Mollard, *J. Phys.* **49**, C8 (1988).
9. H. Zagnazi, M. Malassis, P. Poix, J. Guille, J. C. Bernier, and C. Chaumont, *J. Solid State Chem.* **102**, 40 (1993).
10. M. Pechini, U.S. Patent 3 231 328, 1966.
11. M. Vallet-Regí, P. Rodríguez, X. Obradors, A. Isalgué, J. Rodríguez, and M. Pernet, *J. Phys.* **46**, C6 (1985).
12. L. Pai and P. Lessing, *J. Mater. Res.* **7**, 502 (1992).
13. Z. Zheng, B. Guo, and X. Mei, *J. Magn. Magn. Mat.* **78**, 73 (1989).
14. M. V. Cabañas, J. M. González-Calbet, M. Labeau, P. Mollard, M. Pernet, and M. Vallet-Regí, *J. Solid State Chem.* **101**, 265 (1992).
15. P. Gaud and J. C. Joubert, Eur. Patent Appl. EP 186 603, 1986.
16. J. Thery, *Ann. Chim.* **7**, 207 (1962).
17. M. V. Cabañas, J. M. González-Calbet, and M. Vallet-Regí, *J. Mater. Res.* **9**, 712 (1994).
18. M. Pernet, X. Obradors, M. Vallet, T. Hernández, and P. Germi, *IEEE Trans. Magn.* **24**, 1998 (1988).
19. J. Smit and H. P. J. Wijn, in "Ferrites." Philips Tech. Lib. Centrex Pub., Eindhoven, 1959.
20. H. B. G. Casimir, J. Smit, H. Enz, J. F. Fast, H. P. J. Wijn, F. W. Gorter, A. J. W. Duyvesteyn, J. D. Fast, and J. J. de Young, *J. Phys. Radium* **20**, 360 (1959).
21. X. Batlle, J. Rodríguez, X. Obradors, M. Pernet, M. Vallet, and J. Fontcuberta, *J. Phys.* **49**, C8 (1988).
22. X. Batlle, X. Obradors, J. Rodríguez, M. Pernet, M. V. Cabañas, and M. Vallet, *J. Appl. Phys.* **70**, 1614 (1991).
23. O. Kubo, T. Ido, H. Yokoyama, and Y. Koike, *J. Appl. Phys.* **57**, 4280 (1985).