Magnetic properties of $BaFe_{12-2x}Co_xSn_xO_{19}$ prepared by coprecipitation annealing

P. C. Kuo
Institute of Materials Engineering, National Taiwan University, Taipei 107, Taiwan, Republic of China

Y. D. Yao
Department of Physics, National Chung Cheng University, Chai-Yi 621, Taiwan, Republic of China and Institute of Physics, Academia Sinica, Taipei 115, Taiwan, Republic of China

W. I. Tzang
Institute of Materials Engineering, National Taiwan University, Taipei 107, Taiwan, Republic of China

The chemical coprecipitation annealing method is shown to be suitable for preparing $BaFe_{12-2x}Co_xSn_xO_{19}$ powders with a hexagonal fine platelet structure and a narrow particle size distribution. The proper annealing temperatures are between 800 and 900 °C. The saturation magnetization decreases slowly with increasing x; however, the coercivity decreases rapidly with increasing x. When $x=0.8$, the coercivity is reduced to below 1000 Oe, while the value of the saturation magnetization is near 52 emu/g. The temperature coefficient of coercivity decreases roughly from 2.6 to -1.0 Oe/°C, when x increases from 0.0 to 1.2.

I. INTRODUCTION

Barium ferrite particles with the substitution of Fe by appropriate metals, especially Co and Ti, have been shown to be promising candidates for high density magnetic recording.[1–5] It is well known that, due to the high magnetocrystalline anisotropy, pure Ba ferrite with a hexagonal platelet morphology exhibits a coercivity that is too high for magnetic recording purposes. The total anisotropy of the barium ferrite is the sum of the crystalline and shape anisotropies; and they are orthogonal to each other.[6] Thus, the crystalline anisotropy encourages magnetization along the hexagonal axis, while the shape anisotropy supports magnetization in the basal plane. Since both the crystalline and shape anisotropies contribute to the coercivity of the particles; the coercivity can be adjusted by varying both the kind and amount of the substituents, and the size and shape of the particles. Generally speaking, the size and shape of the particles will depend on the synthesis procedures. Several synthesis procedures have been proposed to obtain particles of the appropriate size. Among these are the glass crystallization method,[7] the hydrothermal synthetic method,[8] the chemical coprecipitation method,[9] and the liquid mix technique.[10]

The studies of Sn as one of the substituents for Fe in Ba ferrite by the glass crystalization method,[7] by the liquid mix technique[10] and by the modified citrate method[11] have been reported recently. Sn has been reported to be an effective substituent in improving the temperature coefficient of coercivity for Co-Ti substituted Ba ferrite. Therefore, it would be very interesting to study the properties of $BaFe_{12-2x}Co_xSn_xO_{19}$ fine particles prepared by different methods.

In this investigation, we report the study of the morphological, structural, and magnetic characteristics of $BaFe_{12-2x}Co_xSn_xO_{19}$ fine particles prepared by the chemical coprecipitation annealing method. However, by comparing with the early process, we used NaCl as a flux to avoid the Ba-ferrite particles sintered together during annealing treatment. The other important feature of this method is the intimate mixing of ions at the atomic level, so that subsequent nucleation and crystallization can occur at quite low temperatures. The annealing conditions and the variations of the magnetic properties with Co and Sn substitutents are described below.

II. EXPERIMENT

High purity $BaCl_2.2H_2O$, $FeCl_3.6H_2O$, $CoCl_2.6H_2O$, $SnCl_4.5H_2O$, and Na_2CO_3 were used as starting materials. According to the formula of $BaFe_{12-2x}Co_xSn_xO_{19}$ with x between 0 and 1.2, each Ba-, Fe-, Co-, and Sn-salt solution was prepared by adding appropriate amount of salt into deionized water and stirring to complete dissolution. The Na_2CO_3 solution was prepared by dissolving Na_2Co_3 into deionized water. At first, the separate Ba-, Fe-, Co-, and Sn- solutions were poured together and then mixed slowly with the Na_2CO_3 solution by stirring. The reaction temperature was held always at 30 °C. The resulting dispersed precipitate, which consists of fined divided $BaCO_3$, $Fe_2(CO_3)_3$, $CoCO_3$, and $Sn(CO_3)_2$ in an aqueous solution of sodium chloride, is filtered and dried in vacuum. After drying, the coprecipitated product is an intimate mixture of the carbonates plus solid sodium chloride. Second, this mixture was followed by a heat treatment at a desired temperature named T_H from 590 to 900 °C in air for a proper time called t_H and slowly cooled to room temperature with an adjustable cooling rate. This high temperature reacted products were washed with hot water in order to dissolve the sodium chloride. Finally, it is filtered and dried at 60 °C to obtained Co-Sn substituted Ba-ferrite particles.

Powder x-ray diffraction, transmission electron microscopy (TEM), atomic absorption spectroscopy (AAS), and differential thermal analysis (DTA) were used for

 0021-8979/93/106292-03$06.00

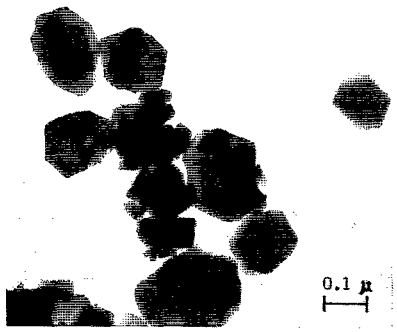

FIG. 1. The transmission electron micrograph of the $BaFe_{10.8}Co_{0.6}Sn_{0.6}O_{19}$ particles.

structure, morphology, particle size, and composition, etc. analyses. The magnetical properties were measured by using a vibrating sample magnetometer (VSM) with a maximum applied field of 20 kOe.

III. RESULTS AND DISCUSSION

During the chemical coprecipitation process, the molar concentration of the ions, and the reaction temperature are very important parameters. We have found that the suitable conditions are as follows: the reaction temperature is 30 °C, and the molar concentration for $[Ba^{2+}]$ should be larger than 0.01 M.

Based on x-ray diffraction, TEM, AAS, and DTA studies, we have successfully synthesized amorphous coprecititated powders with desired composition, which will crystallize to hexagonal platelets after the high temperature heat treatment, for $BaFe_{12-2x}Co_xSn_xO_{19}$ with x between 0 and 1.2.

Generally speaking, the particle size distribution is quite narrow; and the average diameter and aspect ratio for these hexagonal platelets are about 0.15 μm and 4, respectively. An example of a transmission electron micrograph is given in Fig. 1 for $BaFe_{10.8}Co_{0.6}Sn_{0.6}O_{19}$.

The high temperature heat treatment for the final coprecipitated products were between 590 and 900 °C. We found that the suitable time for this high temperature annealing is about 2 h. As an example, the x-ray diffraction patterns, (a)–(e) for $BaFe_{10.4}Co_{0.8}Sn_{0.8}O_{19}$ annealed at 590, 620, 690, 750, and 800 °C, respectively are given in Fig. 2. It is evident that the proper annealing temperature is above 800 °C. Below roughly 800 °C, we always observed some α-Fe_2O_3 phases in many samples studied; and the NaCl peaks in Fig. 2 were disappeared after washing the samples by hot water.

Figure 3 shows the experimental data for the saturation magnetization, M_s, and the coercivity, H_c, at room temperature for all the $BaFe_{12-2x}Co_xSn_xO_{19}$ samples as a

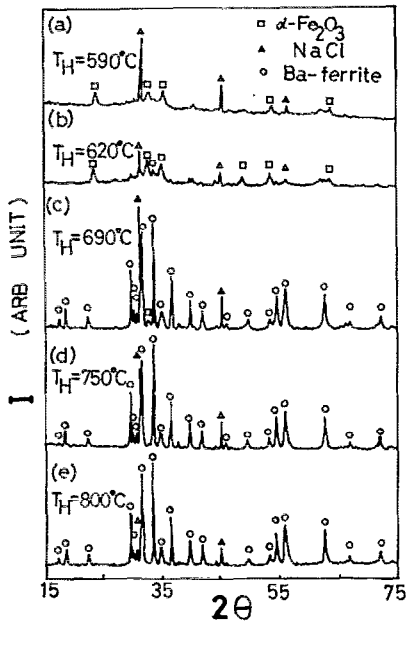

FIG. 2. The x-ray diffraction patterns of the $BaFe_{10.4}Co_{0.8}Sn_{0.8}O_{19}$ powders with different annealing temperatures T_H: (a) 590 °C, (b) 620 °C, (c) 690 °C, (d) 750 °C, and (e) 800 °C.

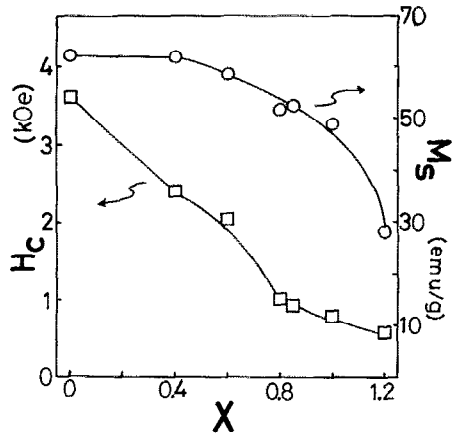

FIG. 3. The saturation magnetization M_s and the coercivity H_c at room temperature for the $BaFe_{12-2x}Co_xSn_xO_{19}$ samples as functions of x.

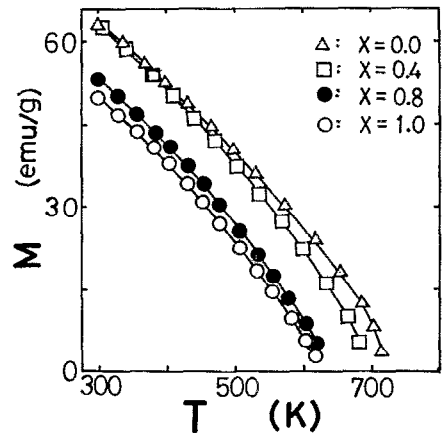

FIG. 4. The saturation magnetization for the $BaFe_{12-2x}Co_xSn_xO_{19}$ samples as a function of temperature between 300 and 800 K.

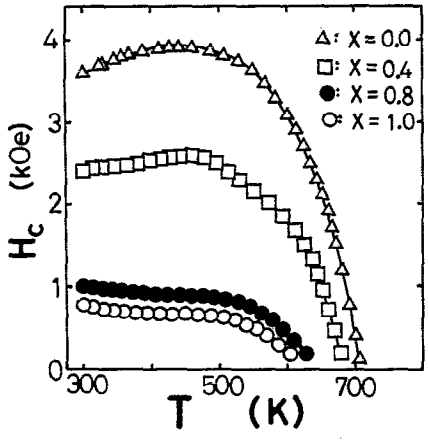

FIG. 5. The coercivity for the $BaFe_{12-2x}Co_xSn_xO_{19}$ samples as a function of temperature between 300 and 800 °K.

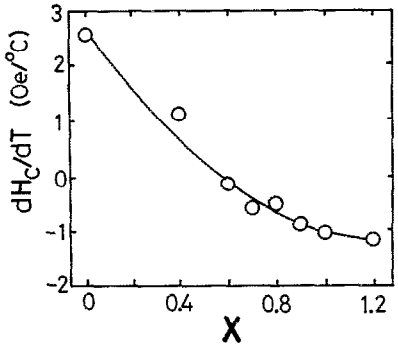

FIG. 6. The temperature coefficient of coercivity for the $BaFe_{12-2x}Co_xSn_xO_{19}$ samples as a function of x.

function of the Co and Sn concentration x. It is clear that the saturation magnetization at room temperature decreases slowly with increasing x; while the coercivity decreases rapidly with increasing x. For example, for sample with $x=0.8$, the coercivity is reduced roughly to below 1000 Oe, however, the value of the saturation magnetization is still 52 emu/g. This is a quite promising condition for using it as a magnetic recording media.

In order to study the nature of the temperature dependence, Figs. 4 and 5 present the M_s and H_c as functions of temperatures between 300 and 800 °K for $BaFe_{12-2x}Co_xSn_xO_{19}$ with $x=0$, 0.4, 0.8, and 1.0. These two figures tell us that the M_s decreases with increasing temperature, and both the H_c and the Curie temperature, T_c, decrease with increasing the Co and Sn concentration x. Here, the temperature dependent behaviors of M_s are not properly to use for the determination of T_c; however, we can roughly say that by comparing the temperature dependence of both M_s and H_c it is quite reasonable. And our experimental results are also qualitatively consistent with those previous reports.[7,10,11]

The temperature coefficient of the coercivity, defined by dH_c/dT, was determined between 300 and 370 °K. The values of dH_c/dT for the $BaFe_{12-2x}Co_xSn_xO_{19}$ samples as a function of the Co and Sn concentration x are presented in Fig. 6. We notice that the value of dH_c/dT of our samples decreases from $+2.6$ to -1.0 Oe/°C by increasing the Co and Sn concentration x from 0.0 to 1.2. The sign of the temperature coefficient of coercivity changes from positive for $x<0.6$ to negative for $x\geqslant 0.6$.

In summary, we have shown experimentally that the Co-Sn substituted Ba ferrites with good quality can be synthesized by the chemical coprecipitation annealing method. The advantage of this method is that: First, the Ba-ferrite particles can be fabricated at quite low heat treatment temperature ($\sim$800 °C). Second, due to the formation of NaCl in this process, the fine Ba-ferrite particles can be easily obtained by dissolving NaCl with hot water. We have shown that if x is roughly around 0.8, the magnetic properties of $BaFe_{12-2x}Co_xSn_xO_{19}$ fine particles with a hexagonal platelet structure are suitable for high density magnetic recording.

ACKNOWLEDGMENTS

This work was supported in part by the National Science Council of ROC through Grant Nos. NSC81-0208-M-194-010.

[1] O. Kubo, T. Ido, and H. Yokoyama, IEEE Trans. Magn. **MAG-18**, 1122 (1982).
[2] T. Fujiwara, IEEE Trans. Magn. **MAG-21**, 1480 (1985).
[3] M. P. Sharrock, IEEE Trans. Magn. **MAG-25**, 4374 (1989).
[4] P. Görnert, E. Sinn, W. Schüppel, H. Pfeiffer, M. Rösler, Th. Schubert, M. Jurisch, and R. Sellger, IEEE Trans. Magn. **MAG-26**, 12 (1990).
[5] G. Bate, J. Magn. Magn. Mater. **100**, 413 (1991).
[6] D. E. Speliotis, IEEE Trans. Magn. **MAG-22**, 707 (1986).
[7] O. Kubo, T. Nomura, T. Ido, and H. Yokoyama, IEEE Trans. Magn. **MAG-24**, 2859 (1988).
[8] H. Kaneda, C. Miyakawa, and H. Kojima, J. Amer. Ceram. Soc. **57**, 354 (1974).
[9] W. Roos, J. Amer. Ceram. Soc. **63**, 601 (1980).
[10] M. Pernet, X. Obradors, M. Vallet, T. Hernandez, and P. Germi, IEEE Trans. Magn. **MAG-24**, 1898 (1988).
[11] U. Meisen and A. Eiling, IEEE Trans. Magn. **MAG-26**, 21 (1990).