Preparation of Magnetic BaFe$_{12}$O$_{19}$ Fine Powder via Metallic Esters Precursors

(   )

200 nm

923K

1073K

Abstract (Keywords: barium ferrite, precursor method, magnetic ceramics)

Ultrafine BaFe$_{12}$O$_{19}$ powder with crystallite sizes less than 200 nm was prepared via a citric acid precursor method. Citric acid was added into an aqueous solution, containing nitrates of Ba^{2+} and Fe^{3+} in a stoichiometric ratio to form barium ferrite, to chelate metallic ions in the solution. The pH of aqueous solutions was adjusted using NH$_4$OH. After adding ethylene glycol into the solution and raising the system temperature, esterification and dehydratation led to the formation of solid ester-precursor. The distribution and contents of metallic ions in the ester are affected by the [citric acid]/[metallic ions] molar ratio used and the pH of starting solutions. By using the ester-precursor obtained at pH = 9 with [citric acid]/[metallic ions] = 1.5, crystalline BaFe$_{12}$O$_{19}$ was appeared at temperatures as low as 923 K and pure barium ferrite was obtained at 1073 K. According to the experimental results obtained, the reaction mechanism involved in the pyrolysis of esters was proposed and discussed.

I. INTRODUCTION

Barium ferrite with hexagonal molecular structure (BaFe$_{12}$O$_{19}$) is well established as a high performance permanent magnetic material[1], owing to its fairly large magnetocrystalline anisotropy, high Curie temperature, and relatively large magnetization, as well as excellent chemical stability and corrosion resistivity. In recent years, barium ferrite has been extensively studied for advanced recording applications, such as disk drivers and video recorders[2, 3].

The characteristics of BaFe$_{12}$O$_{19}$ particles are very important for manufacturing permanent ceramic magnets because of their influence on the quality of final products. Several non-conventional techniques, such as the co-precipitation method[4-6], the glass crystallization method[7-9], the hydrothermal technique[10] and the precursor method[11,12], have been used or are under development for preparing ultrafine barium ferrite particles. The most important feature of these methods is to use liquid media to intimately mix the required metallic constituents on an ionic level. Mixing the required metallic ions homogeneously in atomic scale can form the required oxide phase(s) at relatively low temperatures, resulting in small particles.

In this study, a precursor method was used to prepare barium ferrite powder. In preparation, citric acid was adopted as chelating agent for metallic ions and after esterification and pyrolysis, submicron barium ferrite powder was produced and characterized.

II. EXPERIMENTAL PROCEDURE

Ba(NO$_3$)$_2$ and Fe(NO$_3$)$_3$.9H$_2$O, in a stoichiometric ratio to form BaFe$_{12}$O$_{19}$, were dissolved in de-ionized water to form the required aqueous solution of 0.04M. To chelate Ba^{2+} and Fe^{3+} in the solution, citric acid was added into the prepared aqueous solution. The pH of solutions was adjusted using NH$_4$OH and varied from ~1 to 9. Esterification of the solution was carried out by introducing ethylene glycol into the solution and raising the solution temperature to 353 K. The amount of ethylene glycol added was 1.5 times of the number of moles of citric acid in the solution. Esterification in the solution was likely through polycondensation mechanisms since citric acid (with three carboxylic groups) and ethylene glycol (with two hydroxyl groups) are polyfunctional acid and alcohol, respectively. Esterification and solvent evaporation at 353 K resulted in a highly viscous liquid. The viscous liquid was then dried at 393 K in an oven. It is to be noted that volume of the specimen obtained with the addition of NH$_4$OH in

the starting solution was dilated during drying. After drying, the porous solid ester-precursors were obtained.

The solid ester-precursors were pyrolyzed at 623 K, followed by different heat treatment temperatures (i.e., 923, 973, 1073, and 1173 K). The heated specimens were then characterized using XRD, SEM, TEM, TGA, and DSC. Effects of pH and [citric acid]/[metallic ions] molar ratio of the starting solution, as well as heating temperatures, on the characteristics of resultant particles were studied.

III. RESULTS AND DISCUSSION

Figure 1 gives XRD patterns of the particles obtained at 1073 K using four different pH values of the starting solution. For these specimens, molar ratios of citric acid to metallic ions in starting solutions were fixed at 1.5. At pH = ~1 (i.e., no NH_4OH were added to the starting solution.), the particles were composed of α–Fe_2O_3, $BaFe_{12}O_{19}$, and BaO. At pH = 7 and 9, pure $BaFe_{12}O_{19}$ particles were obtained. Raising the pH of starting solutions by adding NH_4OH not only increased the amount of $BaFe_{12}O_{19}$ in particles but also increased the crystallinity of barium ferrites. The degree of chelation of metallic ions, by carboxylic groups ($COOH^-$), in the starting solution is responsible for the uniformity of metallic constituents in the ester-precursor after esterification. At higher pH conditions, more citric acid is ionized, more carboxylic groups can be available to chelate the metallic ions in the solution, and higher uniformity of metallic elements in the ester can be attained. Figure 2 shows TEM photomicrographs of the specimens discussed in Figure 1. At pH = 7 and 9, hexagonal plate-like barium ferrite crystallites with sizes less than 200 nm were obtained. It is also evidenced that the sizes of $BaFe_{12}O_{19}$ crystallites increased with pH. SEM analysis indicated that the particles so obtained were agglomerated and the sizes of primary particles were much less than 500 nm.
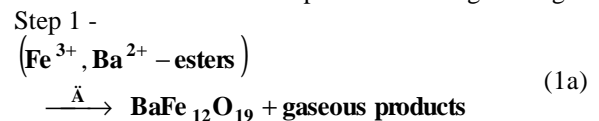
To illustrate the importance of [citric acid]/[metallic ions] molar ratio in the starting solution on the characteristics of derived particles, the molar ratio of citric acid to metallic ions in starting solutions was reduced to 0.5 and the experiment was repeated. Figure 3 is XRD patterns of the specimens so obtained after thermally treating at 1073 K for 3 hrs. Regardless of pH of the starting solution used, all particles were composed of α–Fe_2O_3, $BaFe_{12}O_{19}$, and BaO. At pH = ~1, 3, and 7, α–Fe_2O_3 was the major crystalline phase. The amount of crystalline $BaFe_{12}O_{19}$ increased with pH. The results indicated that at higher pH conditions $BaFe_{12}O_{19}$ is easier to form, which is due to the more completion of chelation of the metallic ions in the solution. Although at pH = 9 barium ferrite became the major phase in particles, α–Fe_2O_3 was still detected in this specimen. This result was ascribed
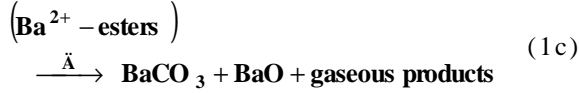
to the deficiency of citric acid in the solution to provide enough carboxylic groups to chelate the required metallic ions.

Effects of the heating temperature for ester-precursors on the derived particles can be demonstrated in figure 4. The specimens were all prepared at pH = 9 with [citric acid]/[metallic ions] = 1.5 but subjected to different heating temperatures. At 623 K, tiny γ–Fe_2O_3, BaO, and $BaCO_3$ crystallites were detected. $BaFe_{12}O_{19}$ crystallites appeared at 923 K and became the major phase in particles after 973 K. At 923 K, γ-Fe_2O_3 allotropically transformed to α-Fe_2O_3. After 1073 K, only crystalline $BaFe_{12}O_{19}$ was detected. XRD analysis indicated that during heat treatment $BaCO_3$ was formed as an intermediate phase and disappeared at 1073 K or above, implying that $BaCO_3$ decomposed at temperatures around 1073 K. Although $BaFe_{12}O_{19}$ formed at 923 K, pure barium ferrite particles could not be obtained before the complete decomposition of $BaCO_3$.
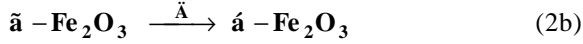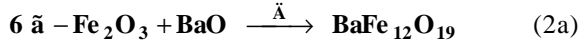
To find out the exact temperature range for $BaCO_3$ decomposition, the specimen heated at 623 K was thermally analyzed using DSC and TGA. Figure 5 gives the corresponding thermal curves, using a heating rate of 10 ^{o}C/min and operating in stagnant air. Between 523 and 773 K, the sample experienced exothermic changes and the sample weight reduced about 11%. These exothermic changes were mainly due to the decomposition of esters. This indicates that heating the ester-precursor at 773 K or above is necessary for complete decomposition of the esters prepared in this experimental condition. Depending on the interactions between metallic ions and carboxylic groups and the amounts of carboxylic groups and ethylene glycol available in the system, esters with different molecular weights and metal contents may be produced during esterification. Esters with different molecular weights and metal contents will give a wide temperature range for esters decomposition. Another exothermic change accompanied with slight weight loss was occurred at temperatures between 973 K and 1073 K. By comparing the results obtained from the thermal analysis and XRD (refer to figure 4 and figure 5), it is evidenced that intermediate $BaCO_3$ phase decomposed at 973 ~ 1073 K during heating.

According to the experimental results obtained in this study, it was postulated that after esterification and dehydration, the following reaction steps would occur in the obtained solid precursor during heating:
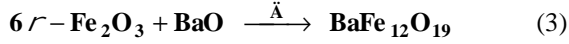
Step 1 -

$$\left(Fe^{3+}, Ba^{2+} - esters\right)$$
$$\xrightarrow{\ddot{A}} BaFe_{12}O_{19} + gaseous\ products \tag{1a}$$

$$\left(Fe^{3+} - esters\right)$$
$$\xrightarrow{\ddot{A}} \tilde{a} - Fe_2O_3 + gaseous\ products \tag{1b}$$

$$\left(Ba^{2+} - esters\right) \xrightarrow{\ddot{A}} BaCO_3 + BaO + gaseous\ products \qquad (1c)$$

Step 2 -

$$6\ \tilde{a} - Fe_2O_3 + BaO \xrightarrow{\ddot{A}} BaFe_{12}O_{19} \qquad (2a)$$

$$\tilde{a} - Fe_2O_3 \xrightarrow{\ddot{A}} \acute{a} - Fe_2O_3 \qquad (2b)$$

$$BaCO_3 \xrightarrow{\ddot{A}} BaO + CO_2 \qquad (2c)$$

Step 3 –

$$6\ \digamma - Fe_2O_3 + BaO \xrightarrow{\ddot{A}} BaFe_{12}O_{19} \qquad (3)$$

$\left(Fe^{3+} - esters\right)$ and $\left(Ba^{2+} - esters\right)$ denote that metallic ions in the polyester are mainly ferric ions and barium ions, respectively. $\left(Fe^{3+}, Ba^{2+} - esters\right)$ represents that ferric and barium ions, in the stoichiometric ratio to form hexagonal barium ferrite, are uniformly distributed in the ester. The pyrolysis of organic esters would produce gaseous products; depending on elements in the ester and heating temperatures, CO, CO_2, H_2O, and/or NO_x may be evolved. According to the distribution and contents of metallic elements in esters, the prepared solid precursor firstly decomposes to form $BaFe_{12}O_{19}$, γ-Fe_2O_3, BaO, or $BaCO_3$. The decomposition of esters starts at about 523 K and the resulted $BaFe_{12}O_{19}$ should be in non-crystalline form. Non-crystalline $BaFe_{12}O_{19}$ will crystallize when the temperature increases. While γ-Fe_2O_3 transforms to α-Fe_2O_3 during further heating, some γ-Fe_2O_3 reacts with adjacent BaO to form barium ferrite. At temperatures around 973 K, $BaCO_3$ begins to decompose. At 1073 K or above, α-Fe_2O_3 reacts with BaO to form $BaFe_{12}O_{19}$.

IV. CONCLUSIONS

This study showed that pure submicron $BaFe_{12}O_{19}$ particles with crystallite sizes less than 200 nm could be produced by pyrolyzing the corresponding ester-precursor at 1073 K or above. The molar ratios of citric acid to metallic ions and the pH of starting solutions used in preparation strongly affect the uniformity of metallic ions distributed in the prepared ester-precursor. Increasing the molar ratio of citric acid to metallic ions and the pH of starting solutions increase the degree of chelation of the metallic ions in the solutions, which leads to metallic ions distributed more uniformly in the ester. The distribution and contents of metallic ions in the ester-precursor are key factors to the formation of high purity of barium ferrite powder. The results also indicated that eliminating $BaCO_3$ intermediate formation during pyrolysis is capable of forming pure $BaFe_{12}O_{19}$ powder at a temperature as low as 923 K.

REFERENCES

1. T. Fujiwara, *IEEE Trans. on Magn.* **21**, 1480 (1985).
2. M. Imamura, Y. Ito, M. Fujiki, T. Hasegawa, H. Kubota, and T. Fujiwara, *IEEE Trans. on Magn.* **22**, 1185 (1986).
3. K. Yamamori, T. Suzuki, and T. Fujiwara, *IEEE Trans. on Magn.* **22**, 1188 (1986).
4. S.E. Jacobo, M.A. Blesa, C. Domingo-Pascual, and R. Rodpiguez-Clemente, *J. Mater. Sci.* **32**, 1025 (1997).
5. Z. Zheng, B. Guo, and X. Mei, *J. Magn. Magn. Mat.* **78**, 73 (1989).
6. W. Roos, *J. Am. Ceram. Soc.* **63**, 601 (1980).
7. B. T. Shirk and W. R. Buessem, *J. Am. Ceram. Soc.* **53**, 192 (1970).
8. E. Lucchini, S. Meriani, and G. Slokar, *J. Mater. Sci.* **18**, 1331 (1983).
9. O. Kubo, T. Ido, and H. Yokoyama, *IEEE Trans. Magn.* **18**, 1122 (1982).
10. D. Barb, L. Diamandescu, and A. Rusi, *J. Mater. Sci.* **21**, 1118 (1986).
11. D. Bahadur, W. Fischer, and M.V. Rane, *Mater. Sci. and Engr.* **A252**, 109 (1998).
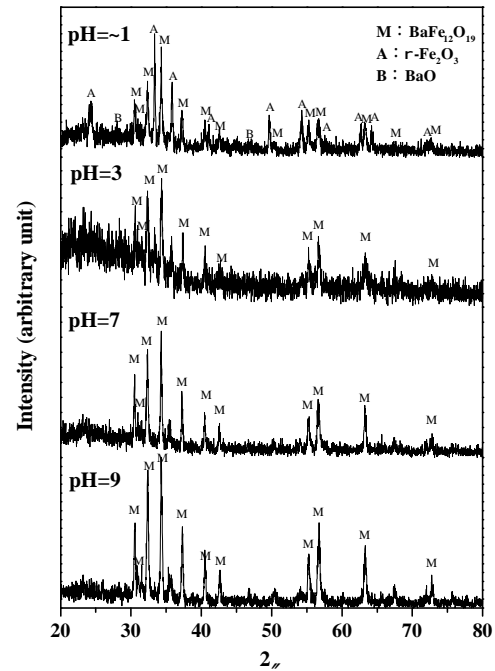12. L. Tai and P.A. Lessing, *J. Mater. Res.* **7**, 502 (1992).

Figure 1. XRD patterns for the specimens ([citric acid]/[metallic ions] = 1.5) obtained at 1073 K, using four different pH values of the starting solution.
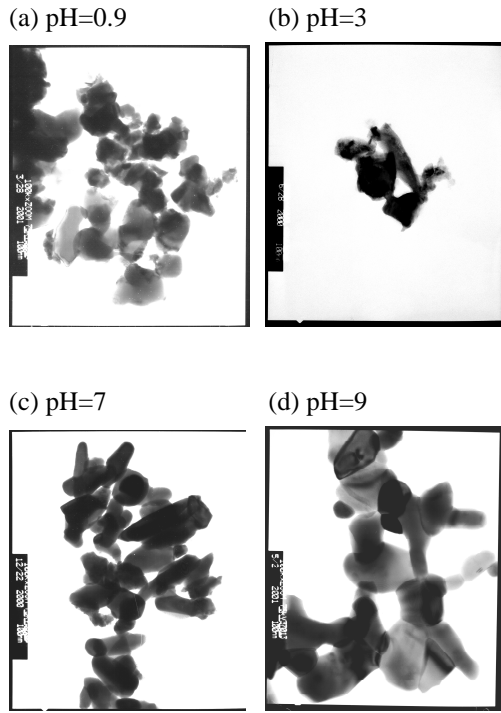
(a) pH=0.9

(b) pH=3

(c) pH=7

(d) pH=9

Figure 2. TEM (× 100 K) photomicrographs for the specimens ([citric acid]/[metallic ions] = 1.5) obtained after 1073 K, using the starting solution of (a) pH = ~ 1, (b) pH = 3, (c) pH = 7, and (d) pH = 9.
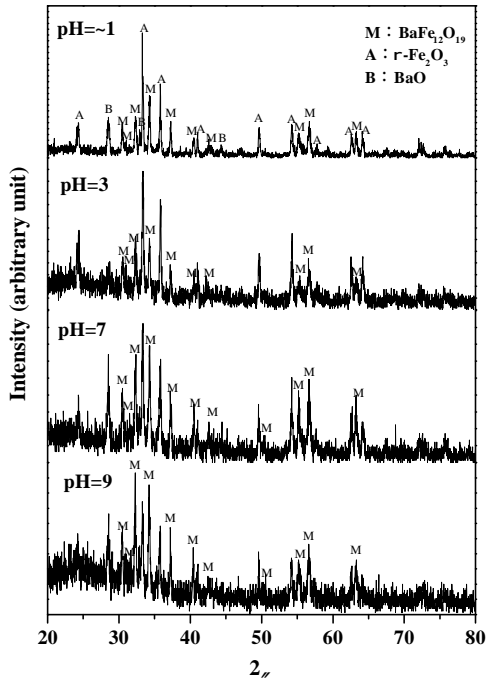
Figure 4. XRD patterns for the specimens ([citric acid]/[metallic ions] = 1.5 and pH = 9) obtained at different pyrolyzing temperatures.

Figure 3. XRD patterns for the specimens ([citric acid]/[metallic ions] = 0.5) obtained at 1073 K, using four different pH values of the starting solution.
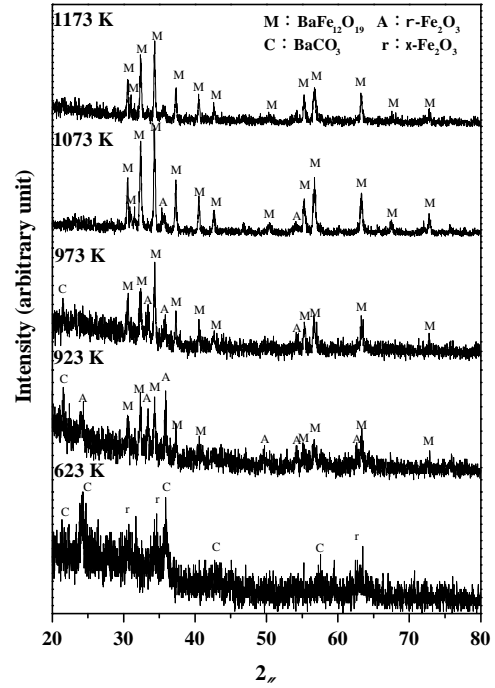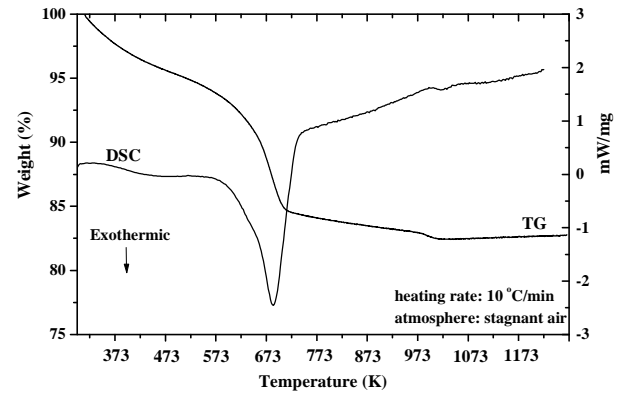
Figure 5. TG and DSC curves for the specimen ([citric acid]/[metallic ions] = 1.5 and pH = 9) obtained at 623 K.