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Author(s)	KIKKAWA, Shinichi; AIBA, Kentaro; MASUBUCHI, Yuji et al.
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Journal of the Ceramic Society of Japan 117 [1] 15-17 2009 **Paper**

Iron source effect on $BaFe_{12}O_{19}$ preparation through citrate route

Shinichi KIKKAWA,† Kentaro AIBA, Yuji MASUBUCHI and Isao SAEKI*

Graduate School of Engineering, Hokkaido University, N13W8, Sapporo 060−8628
***Department of Materials Science and Engineering, Muroran Institute of Technology, 27−1, Mizumoto-cho, Muroran 050−8585**

Both magnetization and coercivity should be controlled on $BaFe_{12}O_{19}$ for its usage in magnetic recording. Preparation of $BaFe_{12}O_{19}$ was studied in citrate route by changing the kinds of iron source. Stoichiometric mixtures of iron compounds with $Ba(NO_3)_2$ were dissolved in distilled water. They were mixed with citric acid aqueous solution and then condensed on a hot plate to their gelatinous products. Their prefired products below 450°C were pelletized and then fired in a temperature range between 750 and 900°C. The product from iron nitrate was a mixture of α-Fe_2O_3, $BaFe_2O_4$ and a small amount of $BaFe_{12}O_{19}$. The product from $Fe(acac)_3$ was pure $BaFe_{12}O_{19}$ fine powder with a crystallite size of < 90 nm. The fine powdered product at 850°C had a saturation magnetization of 58.5 emu·g^{-1}and a coercivity of 5.5 kÖe.

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Key-words : $BaFe_{12}O_{19}$, Iron acetyl, Acetonato, Citrate

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1. Introduction

Barium hexaferrite $BaFe_{12}O_{19}$ is a magnetic material with great scientific and technological interest. It has a relatively high Curie temperature, high coercive force and high magnetic anisotropy field as well as an excellent chemical stability.[1)] Its particle size is important to obtain appropriate value of its magnetic coercivity. Combustion synthesis is very useful to obtain fine powdered sample.[2)] There have been several reports on combustion synthesis of $BaFe_{12}O_{19}$ through citrate route.[3)–7)] Preparation conditions have been tried to adjust by changing citric acid/nitrate ratio,[3)] Ba/Fe ratio, reaction temperature[4)] and pH value in chelation by citric acid.[5)] An introduction of chloride flux has also been discussed.[6)] Their as-burnt products were mixtures of α-, γ-Fe_2O_3 and $BaCO_3$.[3),5)] Their successive firing was needed up to 900°C to obtain pure $BaFe_{12}O_{19}$.[4)]

Homogeneous mixing of Ba^{2+} and Fe^{3+} is very important to obtain pure $BaFe_{12}O_{19}$. Citrate ligand was suggested to be effective at high pH value.[5)] Ferric ions are hydrolyzed to form iron hydroxide at high pH. Stabilization of ferric ion is crucial to obtain homogeneous mixing of Ba^{2+} and Fe^{3+} in aqueous solution at high pH. Sol–gel synthesis of $BaFe_{12}O_{19}$ through citrate route has been studied by changing precursors and thermal treatments.[7)] Either $Fe(NO_3)_3{\cdot}9H_2O$ or $Fe(OH)_3$ and either $Ba(NO_3)_2$ and $BaCO_3$ were used as their precursors in the study. Removal of NO_3^- was important to obtain $BaFe_{12}O_{19}$. There has been no further discussion about stable iron source against its hydrolysis.

In the present study, the use of iron acetyl acetonato was studied to obtain pure $BaFe_{12}O_{19}$ as an iron source in the citrate route.

2. Experimental

Either $Fe(NO_3)_3{\cdot}9H_2O$ or iron acetyl acetonato hereafter denote as $Fe(acac)_3$ of 0.01 mol was dissolved in 25 cm^3 of distilled water. $Ba(NO_3)_2$ was added in a stoichiometric molar ratio of 12:1. Citric acid aqueous solution with various concentration between 0.02–0.8 mol·dm^{-3} was added. The mixed aqueous solutions were heated under stirring on a hot plate to obtain their gels. They were fired to the precursors in a temperature range between 250°C and 450°C for 1 h. Their successive firing was performed at temperatures between 700°C and 950°C for 1 h after their grinding. All the reagents were purchased from Kanto Chemical Co. in purity of 99.0% up.

X-ray diffractometer X'Pert-MPD (Panalytical) with monochromatized Cu Kα radiation was used for phase identification and crystallite size estimation. TG–DTA was measured by using the equipment model 2000 (MAC Science) in a heating rate of 12°C/min. Vibrating sample magnetometer BHV–50 (Riken Denshi) was used for magnetic hysteresis measurements in a magnetic field of ± 15 kÖe. Particle shape and size were observed with SEM (JSM–6300F, JEOL).

3. Results and discussion

3.1 Products from $Fe(NO_3)_3{\cdot}9H_2O$ as iron source

Only $Ba(NO_3)_2$ crystallized in the precursor prepared from $Fe(NO_3)_3{\cdot}9H_2O$ as iron source together with $Ba(NO_3)_2$. The ferric ions were present as X-ray amorphous in it. The fired product at 800°C for 1 h was a mixture of α-Fe_2O_3, $BaFe_{12}O_{19}$ and $BaFe_2O_4$. The α-Fe_2O_3 major phase suggests that the ferric ions formed amorphous either ferric hydroxide or oxyhydroxide in the precursor. The concentration of citric acid was increased from 0.2 to 0.8 mol·dm^{-3} in every 0.2 mol·dm^{-3}. All the fired products were similar mixtures of α-Fe_2O_3, $BaFe_{12}O_{19}$ and $BaFe_2O_4$. Most of the ferric ions might have been hydrolyzed without forming their citrate gel in the aqueous solution. They crystallized as α-Fe_2O_3 in the fired product.

3.2 Products from $Fe(acac)_3$ as iron source

The precursor starting from Fe(acac) as iron source was X-ray amorphous at firing temperature below 200°C. Its TG–DTA measurement showed two exothermic peaks at 257°C and 353°C with a total weight loss of 68%. The fired product at 800°C for

† Corresponding author: S. Kikkawa; E-mail: kikkawa@eng.hokudai.ac.jp

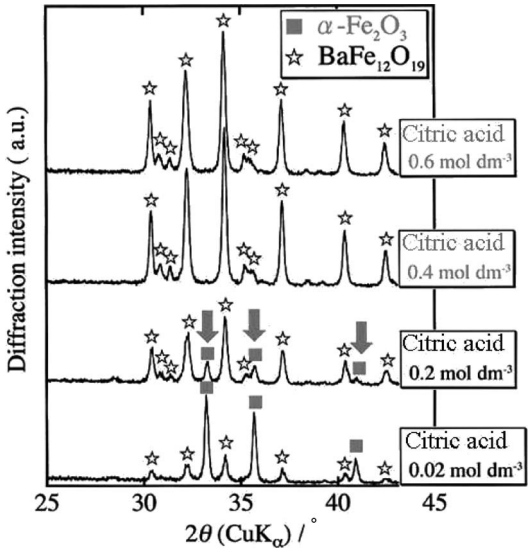

Fig. 1. X-ray diffraction patterns for the fired products at 800°C for 1 h prepared from the $Fe(acac)_3$ derived precursors with various amounts of citric acid prefired at 250°C.

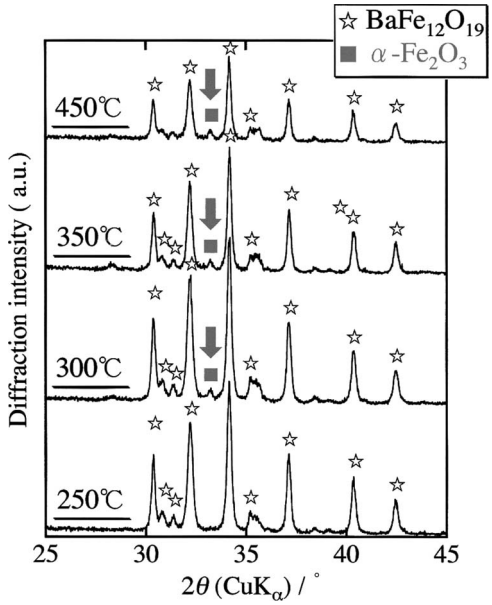

Fig. 2. X-ray diffraction patterns for the fired products at 800°C for 1 h prepared from the $Fe(acac)_3$ derived precursors prefired at various temperatures obtained with citric acid of 0.6 mol·dm^{-3}.

1 h was pure $BaFe_{12}O_{19}$ when the starting mixture was prepared in the citric acid concentration above 0.4 mol·dm^{-3} as shown in **Fig. 1**. Total concentration of Fe^{3+} and Ba^{2+} was 0.21 mol·dm^{-3}. α-Fe_2O_3 impurity appeared in the fired product obtained at the citric acid concentration of 0.2 mol·dm^{-3} or less. The amount of impurity much increased in the product at the concentration of 0.02 mol·dm^{-3}. Enough amount of citric acid is required to obtain homogeneous mixing in the gel even in the usage of $Fe(acac)_3$ as the iron source. Firing the precursor above 300°C led to an appearance of α-Fe_2O_3 impurity in the final fired products at 800°C as shown in **Fig. 2**. Homogeneously mixed amorphous precursor is crucial to obtain pure $BaFe_{12}O_{19}$.

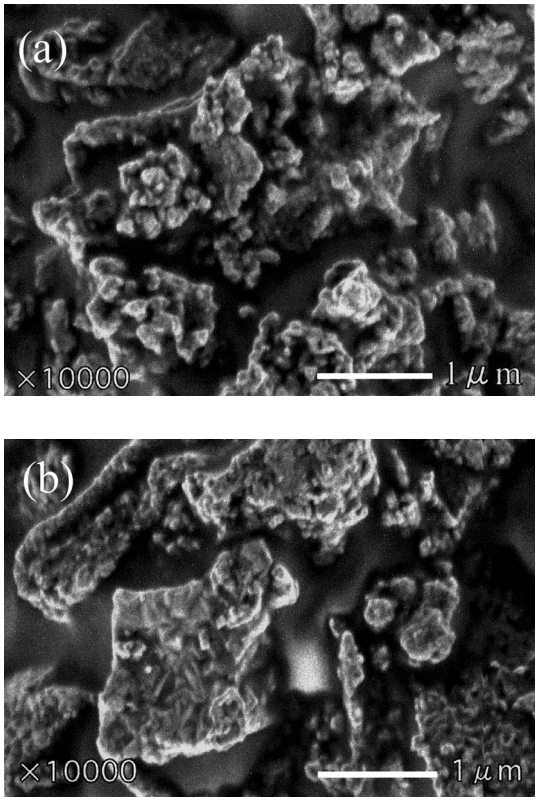

Fig. 3. SEM observation of the fired products at (a) 800°C and (b) 900°C for 1 h.

Magnetic property changed with the final firing temperature. The saturation magnetization reached to the value above 57 emu·g^{-1} at the firing temperature above 800°C. The magnetic coercivity had a maximum value of 5.51 kÖe at the firing temperature of 850°C. The $BaFe_{12}O_{19}$ product had a crystallite size of 97 nm calculated from X-ray diffraction line broadening. The size is around the boundary between single and multi magnetic domains. SEM observation showed the primary crystals of about 100 nm agglomerated to form the secondary crystals of about 1 μm as represented in **Fig. 3**. The latter size grew rapidly with the firing temperature. The saturation magnetization value was 58.5 emu·g^{-1}. The present values were comparable or superior to those for the products prepared in other methods; 20.0 emu·g^{-1} and 3.99 kÖe in crystallization from glass,[8] 64.0 emu·g^{-1} and 2.30 kÖe in hydrothermal method[9] and 70.1 emu·g^{-1} and 5.78 kÖe in firing of the hydrolyzed gel.[7] Homogeneous mixing of Ba^{2+} and Fe^{3+} in aqueous solution accelerated the formation and the crystallization of $BaFe_{12}O_{19}$. The relatively large magnetization value could be attained at low firing temperature in short duration due to the homogeneity in mixing.

As a conclusion, iron acetyl acetonato was useful as the iron source to obtain pure barium hexaferrite without α-hematite impurity in its preparation through citrate route. Its fine powder with appropriate magnetic property was obtained by firing at lower temperature (< 850°C) in shorter duration (< 1 h) than the conventional ceramic method. Its saturation magnetization was 58.5 emu·g^{-1} and coercivity was 5.51 kÖe.

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