

Low temperature synthesis of Sr and Ba M-type ferrites by polymerized complex method

Takeyuki Kikuchi, Tatsuya Nakamura, Makoto Nakanishi*, Tatsuo Fujii*, Jun Takada*,
Yasunori Ikeda**, Mitsunobu Nakamura, Masamichi Miki

Faculty of Engineering, Himeji Institute of Technology, 2167 Syosya, Himeji 671-2201, Japan

Fax: 81-792-67-4926, E-mail: kikuchi@esci.eng.himeji-tech.ac.jp

*Faculty of Engineering, Okayama University, 3-1-1 Tsushima-naka, Okayama 700-8530, Japan

Fax: 81-86-251-8107, E-mail: jtakada@cc.okayama-u.ac.jp

**Institute of Chemical Research, Kyoto University, Uji 611-0011, Japan

Fax: 81-774-38-3118, E-mail: ikedayas@scl.kyoto-u.ac.jp

Synthesis and magnetic properties of M-type hexagonal ferrites with chemical composition of $AFe_{12}O_{19}$ ($A = Ba$ and Sr) were studied. Nitrates of barium, strontium and iron were used as starting materials. The precursor of M-type ferrites was prepared mainly by the polymerization of metal-citric complex with various amounts of ethylene glycol, and heating the gel at 300°C. The precursor was ground, pressed by uniaxial compression in a die and heated at 750 ~ 950°C in air. The phases formed in the samples were determined by powder X-ray diffraction (XRD). Monophasic M-type ferrites were formed at 800°C by polymerized complex method. This formation temperature is lower than the formation temperature by conventional solid-state reaction. Magnetic properties were discussed by measurements of $M-H$ curves with vibration sample magnetometer (VSM). The samples synthesized in this study showed typical $M-H$ hysteresis loop of hard ferrites and large coercive force (6.1 kOe for BaM and 6.9 kOe for SrM). The scanning electron microscope (SEM) was used for morphology observation. The average grain size of M-type ferrites synthesized in this study with plate-like shape was between 50 nm and 100 nm. From these results, large coercive force of the samples in this study is probably caused by achievement of small grain size under the single domain size by polymerized complex method.

Key words: Polymerized complex method, M-type hexagonal ferrite

1. INTRODUCTION

M-type hexagonal ferrite has been widely used as a material of permanent magnets because of their large magnetocrystalline anisotropy, relatively large magnetization, high Curie temperature and chemical stability. For improvement of ferrite magnet, a grain size of ferrite must be small under the size of single magnetic domain. It is considered that the single-domain size for M-type hexagonal ferrites is less than 900 nm and 940 nm for $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$, respectively. However, conventional solid-state reaction requires heat treatment at high temperature (above 1100°C) to obtain monophasic M-type ferrite. Heating at high temperature causes growth of ferrite particles (over 1 μm). Thus, many techniques, such as the co-precipitation method [1,2], the glass crystallization method [3,4], aerosol synthesis [5-7], have been developed to synthesize sub-micron particles of the M-type hexagonal ferrite.

Polymerized complex method has been studied as the technique to synthesize the high quality oxides in the multi-component system, such as High- T_c superconductors [8]. It is considered that the synthesis by polymerized complex method can obtain the desired oxide at low temperature because of mixing the cations homogeneously in atomic scale. Several studies, which adopt similar methods to synthesize the M-type hexagonal ferrite, are reported [9-11]. However, these

studies discussed only preparation of barium ferrite particles, their magnetic properties and microstructures. In our survey among previous articles, the study about formation mechanism of M-type hexagonal ferrite synthesized from the precursor prepared by polymerized complex method is rare [9,11] and in addition, there is no report about synthesis of strontium ferrite by polymerized complex method.

In the present paper, low temperature synthesis and optimization of condition for production of barium and strontium M-type ferrites by polymerized complex method are discussed. Magnetic properties of nanometer-sized ferrite particles are also reported.

2. EXPERIMENTAL PROCEDURE

The precursors of ferrites were prepared by polymerized complex method. High purity reagent of $Ba(NO_3)_2$ (purity of > 99.0%, nacalai tesque), $Sr(NO_3)_2$ (> 98.0% pure, nacalai tesque) and $Fe(NO_3)_3 \cdot 9H_2O$ (> 99.0% pure, nacalai tesque) were used as starting materials. They were dissolved in distilled water with citric acid and ethylene glycol. The nominal molar ratio of the mixed solutions were 1 : 5 : x of metal : citric acid : ethylene glycol with x ranging from 0 to 15. Prepared aqueous solution was heated at 120°C for dehydration and polymerization between metal citrate complex and ethylene glycol. Thermal pyrolysis was

carried out by heating the gel at the temperature range between 250°C and 350°C for 1h in air. The obtained precursor powders were ground with an alumina mortar and compacted by uniaxial pressing into disk specimens, 20 mm in diameter × 1 mm thick, and then heated at temperature range between 750°C and 950°C for 24h in air.

Phase identification and determination of lattice parameters were carried out by powder X-ray diffraction (XRD) (Model RINT-2200/PC, Rigaku), using Cu-K α radiation. Scanning Electron Microscope (SEM) (Model JSM-5310, JEOL) was utilized to investigate the microstructure of the polycrystalline ferrites. Magnetic properties (the saturation magnetization and the coercive force) were discussed by magnetization measurements at room temperature by using a vibration sample magnetometer (Model VSM-5-15, TOEI KOGYO). Magnetization curves of unoriented assemblies of the prepared powders were measured at a maximum applied field of 16 kOe. Cylindrical sample cell, 2.5 mm in diameter and 7.5 mm length, was used and magnetic field was applied axially to minimize the effect of demagnetizing field.

3. RESULTS AND DISCUSSION

3.1 Optimization of starting solution

The optimum condition of starting aqueous solution was investigated mainly about the molar ratio of ethylene glycol. The nominal molar ratio of the mixed solutions were controlled as follows: total amount of metals : citric acid : ethylene glycol = 1 : 5 : x ($0 \leq x \leq 15$).

Figure 1 shows powder X-ray diffraction patterns for barium ferrite powders. These samples were prepared by heating at 800°C for 24 hours in air from precursors with various nominal molar ratio of ethylene glycol. Major product in all the samples is M-type hexagonal ferrite ($\text{BaFe}_{12}\text{O}_{19}$). However, small amount of $\alpha\text{-Fe}_2\text{O}_3$ (hematite) formed as impurity in some of samples. Single phase of M-type hexagonal ferrite is obtained only in the ethylene glycol free sample ($x = 0$).

Figure 2 shows powder X-ray diffraction patterns for strontium ferrite powders. These samples were also prepared by heating at 800°C for 24 hours in air from precursors with various nominal molar ratio of ethylene glycol. Results of strontium ferrites are similar to these of barium ferrites. Major product of the samples is M-type ferrite ($\text{SrFe}_{12}\text{O}_{19}$), and $\alpha\text{-Fe}_2\text{O}_3$ formed as impurity. Monophasic M-type hexagonal ferrite was obtained only under the ethylene glycol free condition.

From the results mentioned above, we can conclude that the optimum condition of starting aqueous solution is the condition without ethylene glycol. By minute investigation about formation process and thermal analysis (TG-DTA), local heating and produce of stable $\alpha\text{-Fe}_2\text{O}_3$ at low temperature were observed as effect of the residual ethylene glycol in the polymerized gel. Details of bad effect of ethylene glycol will be discussed in other publication.

3.2 Magnetic properties

The saturation magnetization, residual magnetization and the coercive force of the prepared ferrite powders

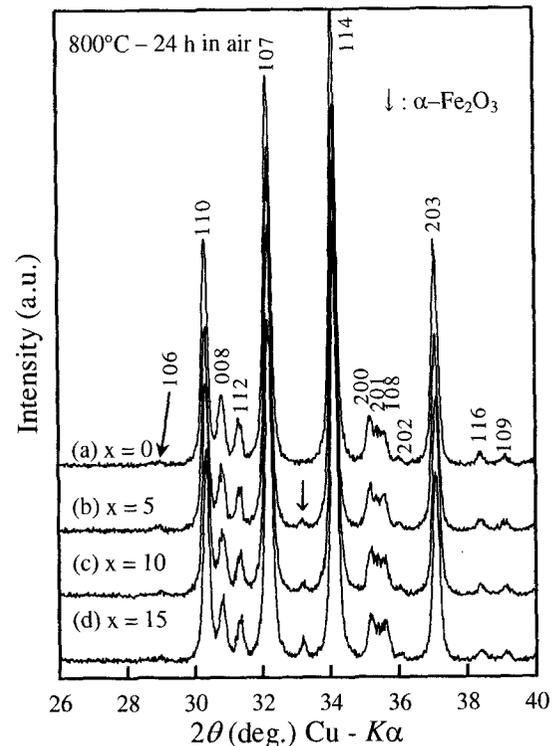


Fig. 1. XRD patterns for barium ferrite powders obtained by heating at 800°C for 24h in air with various nominal molar ratio of ethylene glycol (a) $x = 0$, (b) $x = 5$, (c) $x = 10$ and (d) $x = 15$.

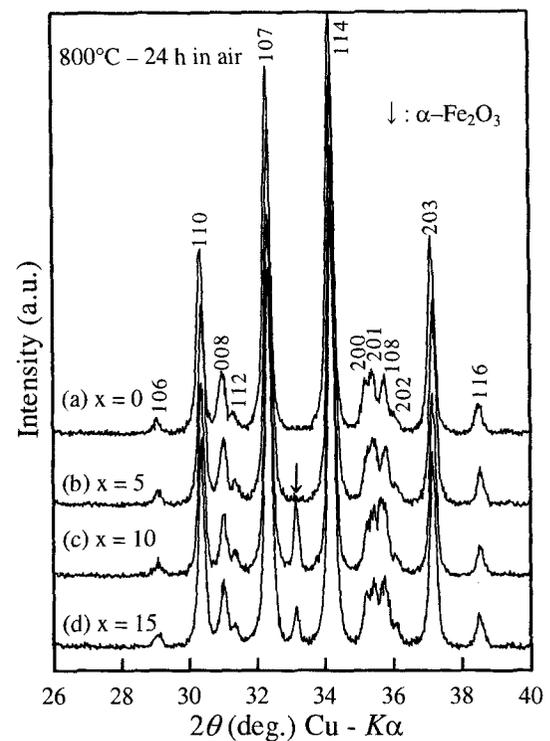


Fig. 2. XRD patterns for strontium ferrite powders obtained by heating at 800°C for 24h in air with various nominal molar ratio of ethylene glycol (a) $x = 0$, (b) $x = 5$, (c) $x = 10$ and (d) $x = 15$.

were discussed from the measured M - H hysteresis loops.

Figure 3 shows the M - H hysteresis loops of barium ferrites (a) and strontium ferrites (b) synthesized by polymerized complex method. The precursors without ethylene glycol were heated at 800°C for 24 hours in air. Results of samples prepared by conventional solid-state reaction (dotted line) are also plotted as references. The samples prepared by solid-state reaction were heated at 900°C (barium ferrite) and 950°C (strontium ferrite) to obtain the single phase of M-type hexagonal ferrite.

From the result in figure 3(a), the barium ferrite powder prepared by polymerized complex method in this study shows extremely improved magnetic properties. This barium ferrite powder exhibited the magnetization at 15 kOe $M(15\text{kOe})$ of 61.4 emu/g, the residual magnetization M_r of 35.3 emu/g and the coercive force H_c of 6.1 kOe (these values of the sample prepared by solid-state reaction are 61.4 emu/g, 35.6 emu/g and 2.5 kOe, respectively). It should be noted that the large coercive force are realized without decreasing of the magnetization by polymerized complex method.

On the other hand, from the result in figure 3(b), the strontium ferrite powder prepared by polymerized complex method showed slight decrease in the saturation magnetization even though extreme increase in the coercive force. Cause of this decrease seems to be due to the increase in volume fraction of surface structure brought by the decrease in grain size (discussed in the following section). This strontium ferrite powder exhibited the magnetization at 15 kOe $M(15\text{kOe})$ of 60.0 emu/g, the residual magnetization M_r of 35.5 emu/g and the coercive force H_c of 6.9 kOe (these values of the sample prepared by solid-state reaction are 62.2 emu/g, 39.3 emu/g and 3.1 kOe, respectively).

Large coercive force determined from magnetization curve shown in fig.3 suggests that large amount of particles in these barium and strontium ferrite powders prepared in this study behave as single magnetic domain grain. It is possible that low temperature synthesis brought small grain size of ferrites and optimization of microstructures. Details of microstructure have been discussed by observation with scanning electron microscope in the following section.

3.3 Microstructure

Figure 4 shows a typical SEM image for the barium ferrite powders synthesized by polymerized complex method. Observed microstructure in the strontium ferrite powders was similar to that of barium ferrite. It is shown that ultra fine particles were produced in this sample, the grain size has a narrow distribution between 50 and 100 nm, and the grain shape is platelet-like. Under SEM observation, when the observed area on the sample stage was randomly scanned, typical microstructure such as fig.4 was seen everywhere. Aspect ratio of horizontal length to perpendicular length was estimated to be small value such as between 3 and 5. From these results, it seems that the improvement of magnetic properties, mainly large coercive force, is brought by not only the effect of increase of single magnetic domain due to small grain size but also the restraint of the shape magnetic anisotropy due to the characteristic grain shape.

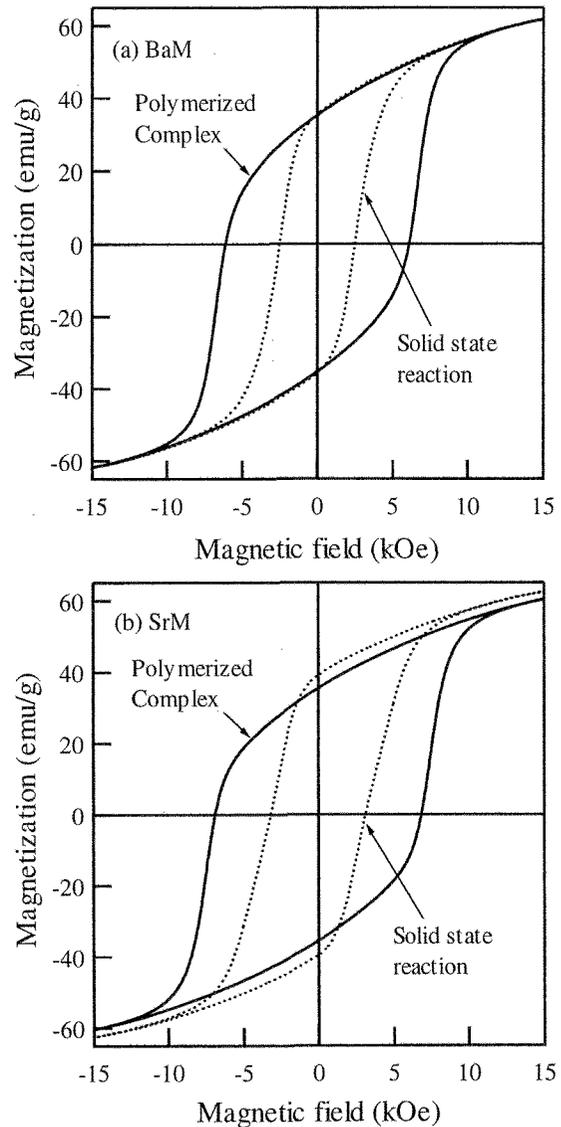


Fig. 3. M - H hysteresis loops of the barium ferrite (a) and strontium ferrite (b) powders synthesized by polymerized complex method. Dotted lines show M - H hysteresis loops of the samples prepared by conventional solid-state reaction.

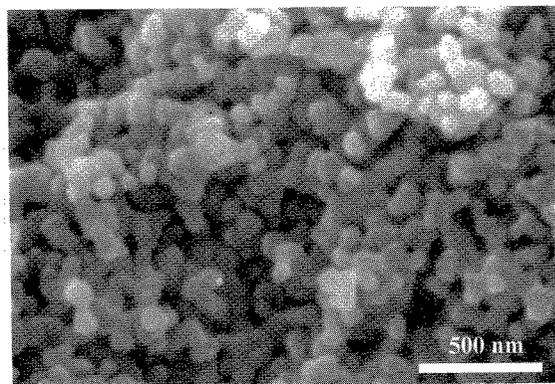


Fig. 4. SEM image for the barium ferrite synthesized at 800°C by polymerized complex method

4. CONCLUSIONS

Low temperature synthesis of the barium and strontium M-type hexagonal ferrites were realized by adopt the polymerization complex method. By optimization of the starting aqueous solution, the single phase of barium and strontium ferrites were obtained at relatively low temperature of 800°C. Optimized condition of starting solution was the condition without ethylene glycol. Low temperature synthesis produced nano-particles (50~100nm) with platelet-like shape of M-type hexagonal ferrites. Resultant powders of barium ferrite and strontium ferrite showed remarkable improvement of magnetic properties, especially large coercive force of 6.1 kOe (barium ferrite) and 6.9 kOe (strontium ferrite). This improvement seems to be due to the effect of small grain size and the grain shape with small aspect ratio.

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