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# Nanosized barium ferrite powders prepared by spray pyrolysis from citric acid solution

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## Abstract

Highly crystalline nanosized barium ferrite ($BaFe_{12}O_{19}$) powders were prepared by spray pyrolysis from a spray solution containing a high concentration of the metal components. The precursor powders obtained from the spray solution containing citric acid were amorphous with a porous and hollow structure. Purely crystalline and fine $BaFe_{12}O_{19}$ powders were obtained after post-treatment between 700 and 1000 °C and subsequent mechanical grinding in an agate mortar. The mean sizes of the powders post-treated at 700 and 1000 °C were 125 and 550 nm, respectively. The specific magnetization of the powders prepared from the spray solution containing citric acid was 57 emu/g.

*Keywords:* A. Powders: gas-phase reaction; A. Powders: chemical preparation; C. Magnetic properties

## 1. Introduction

Barium ferrite ($BaFe_{12}O_{19}$) is used in electronic industries because it is inexpensive and has high coercivity, chemical stability, anisotropy, and corrosion resistance [1–4]. The magnetic properties of $BaFe_{12}O_{19}$ strongly depend on the mean size and microstructure of the powders [5,6]. Nanosized hexagonal $BaFe_{12}O_{19}$ has a single magnetic domain, because of which it has excellent magnetic properties [7]. Therefore, nanosized $BaFe_{12}O_{19}$ powders were prepared using liquid-phase methods such as co-precipitation, sol–gel process, microemulsion, cryochemical method, glycine, and hydrothermal methods [8–13]. Nanosized $BaFe_{12}O_{19}$ powders were also prepared by gas-phase methods. González-Carreño et al. prepared $BaFe_{12}O_{19}$ nanopowders by aerosol pyrolysis, which is commonly known as spray pyrolysis [14]. Nanosized powders were directly prepared by aerosol pyrolysis from an aqueous citrate solution in which the metal concentration was as low as 0.02 M.

In this study, highly crystalline nanosized $BaFe_{12}O_{19}$ powders were prepared by spray pyrolysis from a spray solution containing a high concentration of the metal. The effect of citric acid, which was added as an organic additive to the spray solution, on the morphologies, mean sizes, and magnetic properties of the $BaFe_{12}O_{19}$ powders was also investigated.

## 2. Experimental

The schematic diagram of the spray pyrolysis system used in this study is given elsewhere [15]. The system consists of a droplet generator, a quartz reactor, and a powder collector. A 1.7-MHz ultrasonic spray generator having six vibrators was used to generate a large number of droplets, which were then carried into the high-temperature tubular reactor by a carrier gas. The droplets and powders evaporated, decomposed, and/or crystallized in the quartz reactor [16]. The length and diameter of the quartz reactor were 1200 and 50 mm, respectively. The total concentration of barium nitrate and ferric nitrate was fixed at 0.3 M. After complete optimization of the experimental parameters, it was found that nanosized $BaFe_{12}O_{19}$ powders of the best quality could be obtained at a citric acid concentration of 0.6 M. The flow rate of air, which was used as the carrier gas, was 40 l/min. The crystallinity and morphology of the as-prepared powders obtained by spray pyrolysis at 900 °C were improved after they were post-treated in the box furnace at 500–900 °C in air.

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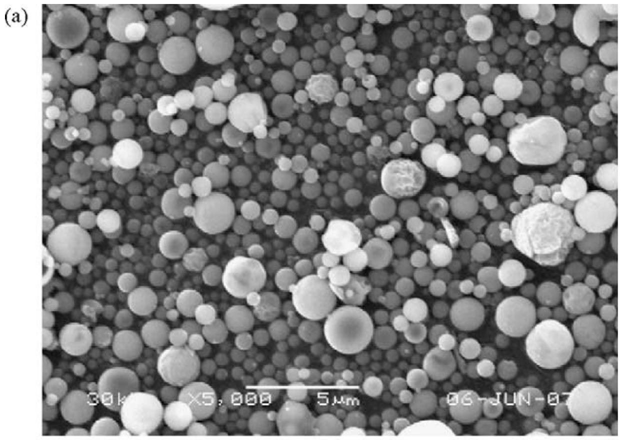
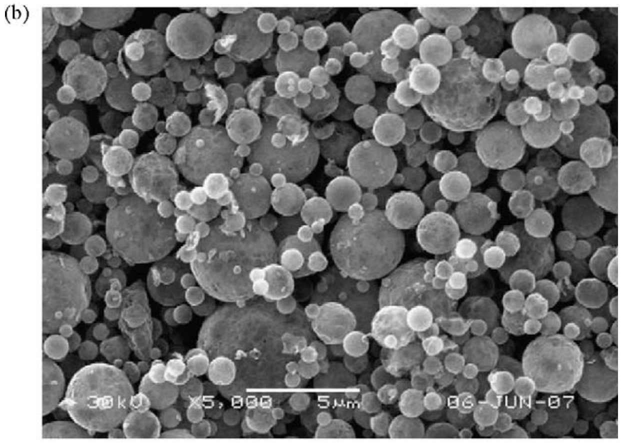
The crystal structures of the as-prepared and post-treated $BaFe_{12}O_{19}$ powders were investigated by X-ray diffractometry (XRD, Rigaku, DMAX-33). The morphological characteristics of the powders were investigated by scanning electron microscopy (SEM, JEOL, JSM 6060). Measurement of the thermal properties of the precursor powders was performed on a thermo-analyzer (TG–DSC; Netzsch, STA409C, Germany) in the temperature range of 40–900 °C (10 °C/min). A vibrating sample magnetometer (VSM; 7300 Lakeshore, USA) was used to measure the saturation magnetization of the $BaFe_{12}O_{19}$ powders as well as the coercive force.

## 3. Results and discussion

The morphologies of the precursor powders prepared by spray pyrolysis from spray solutions with and without citric acid are shown in Fig. 1. All the precursor powders were found to be spherical and micron-sized, irrespective of whether or not citric acid was added to the spray solution. However, citric acid was found to alter the inner structures of the precursor powders. The inner structures of the precursor powders obtained from the spray solution without citric acid were denser than those of the precursor powders obtained from the spray solution with citric acid.



No additive



0.6M CA

Fig. 1. SEM photographs of precursor powders prepared by spray pyrolysis. (a) No additive and (b) 0.6 M CA.

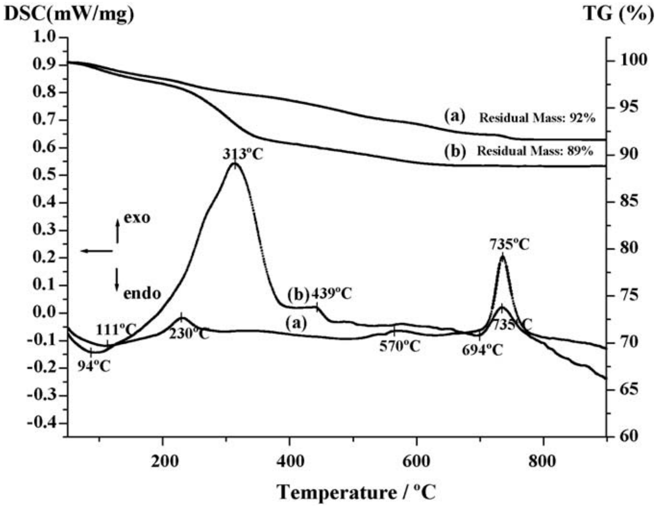
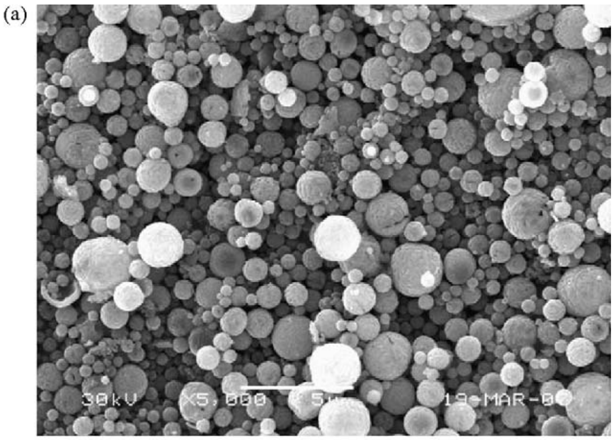
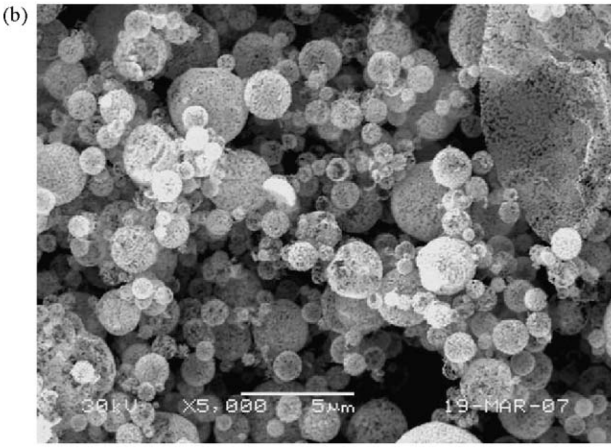


Fig. 2. TG/DSC curves of precursor powders prepared by spray pyrolysis. (a) No additive and (b) 0.6 M CA.

Fig. 2 shows the TG/DSC curves of the precursor powders prepared from the spray solutions with and without citric acid. The TG curves of the precursor powders indicated two weight losses at temperatures below 900 °C. The first prominent



No additive



0.6 M CA

Fig. 3. SEM photographs of $BaFe_{12}O_{19}$ powders post-treated at 800 °C. (a) No additive and (b) 0.6 M CA.

weight loss region from 40 to 200 °C resulted from the loss of adsorbed water. The cause for the second weight loss was different for the precursor powders obtained from spray solutions with and without citric acid. The region of high weight loss from 200 to 400 °C in the TG curves of the precursor powders obtained from the spray solution with citric acid could be attributed to the decomposition of residual carbon components. The exothermic peak at 313 °C in the DSC curve indicated the decomposition of residual carbon components. The DSC curves of the precursor powders prepared from the spray solutions with and without citric acid showed an exothermic peak due to crystallization at 735 °C.

Figs. 3–5 show the SEM micrographs of the $BaFe_{12}O_{19}$ powders post-treated at various temperatures. Fig. 3 shows the SEM micrographs of unground powders that were post-treated at 800 °C. The spherical shape of the precursor powders was maintained even after the post-treatment. The powders obtained from the spray solution without citric acid had filled inner structures. On the other hand, the powders obtained from the spray solution containing citric acid had hollow and slightly aggregated structure of nanometer-sized primary powders. Figs. 4 and 5 show the SEM micrographs of the powders that were manually ground in an agate mortar. The spherical shapes of the powders obtained from the spray solutions without citric acid were maintained after post-treatment at temperatures below 900 °C. Post-treatment at temperatures beyond 1000 °C led to aggregation between the powders and loss of the spherical shape. The $BaFe_{12}O_{19}$ powders obtained from the spray solution with citric acid became non-spherical and fine after grinding. The mean sizes of the powders increased with the post-treatment temperature. The mean sizes of the powders post-treated at 700 and 1000 °C were 125 and 550 nm, respectively.

Figs. 6 and 7 show the XRD patterns of the precursor and post-treated $BaFe_{12}O_{19}$ powders. The precursor powders obtained from the spray solutions with and without citric acid were post-treated at various temperatures. The precursor powders were amorphous, irrespective of the presence of citric acid in the spray solutions; this was attributed to the short residence time of the powders inside the hot-wall reactor. However, the $BaFe_{12}O_{19}$ powders post-treated between 700 and 1000 °C were purely crystalline, irrespective of the presence of citric acid in the spray solutions.

The hysteresis loops of the $BaFe_{12}O_{19}$ powders obtained from the spray solutions with and without citric acid are shown in Fig. 8. The hysteresis loops of the powders post-treated at 800 °C were smooth; this confirmed the formation of pure $BaFe_{12}O_{19}$. The specific magnetizations of the powders prepared from the spray solution with and without citric acid

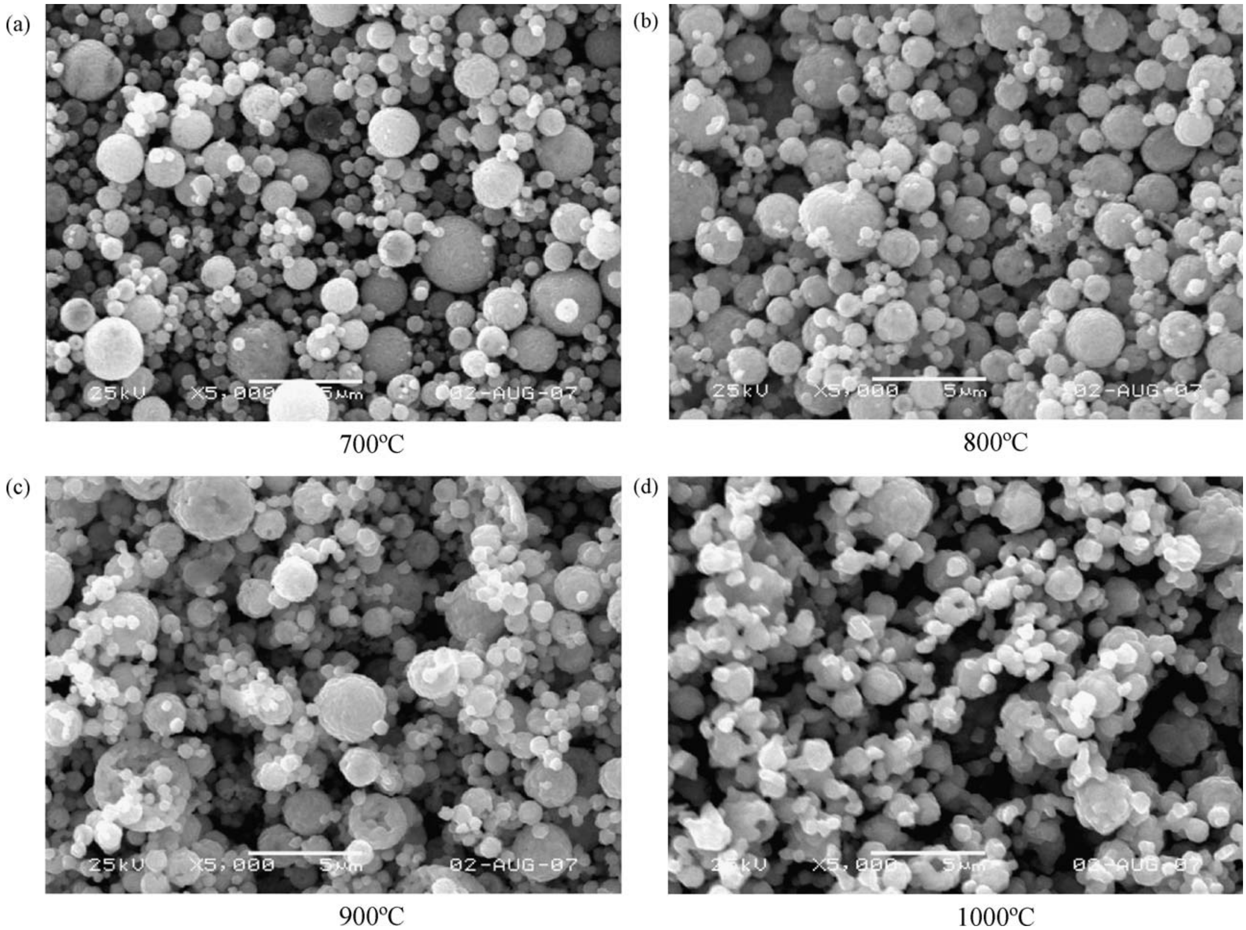
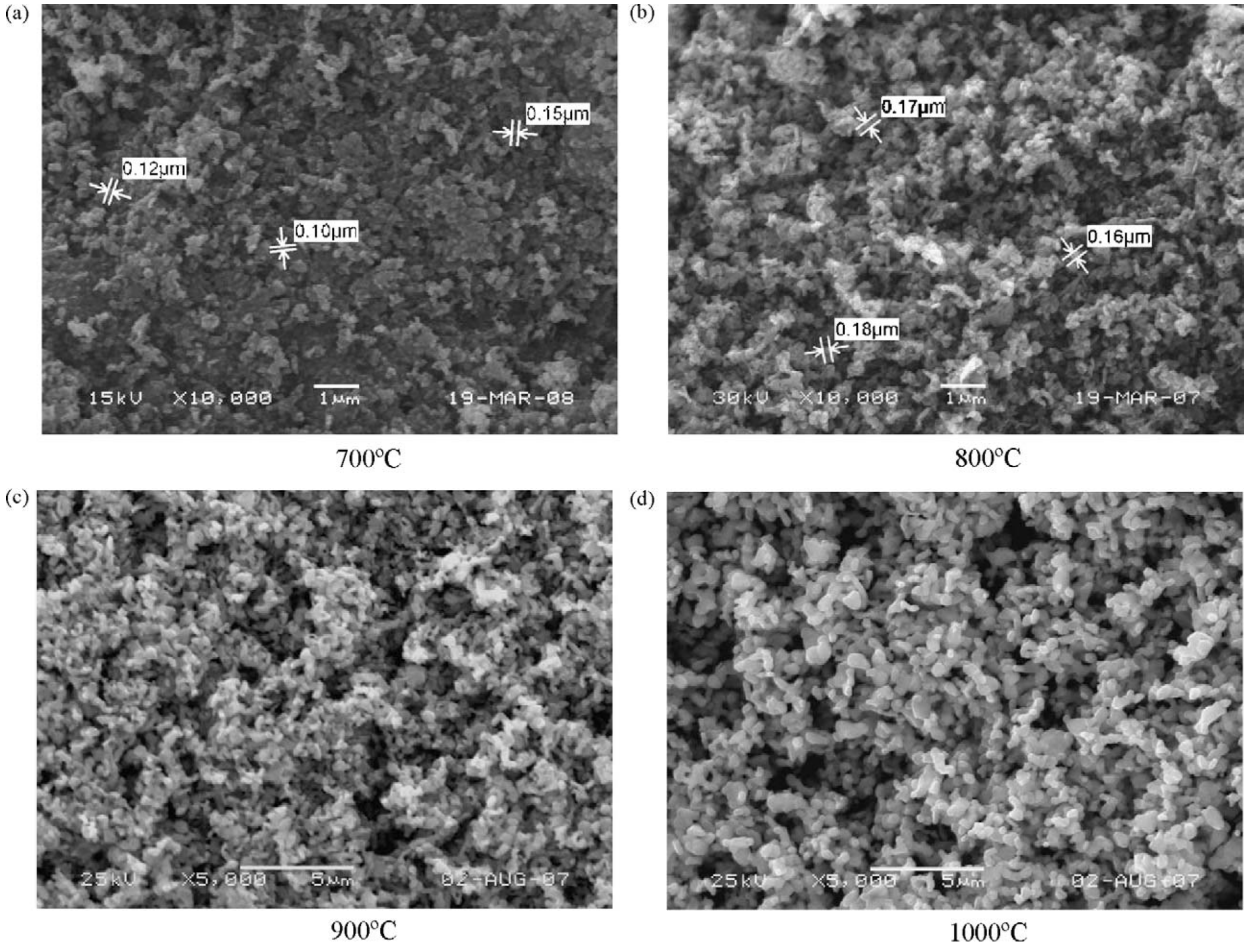


Fig. 4. SEM photographs of post-treated $BaFe_{12}O_{19}$ powders obtained from the aqueous spray solution. (a) 700 °C, (b) 800 °C, (c) 900 °C and (d) 1000 °C.



700°C 800°C

900°C 1000°C

Fig. 5. SEM photographs of the post-treated $BaFe_{12}O_{19}$ powders obtained from the spray solution with CA. (a) 700 °C, (b) 800 °C, (c) 900 °C and (d) 1000 °C.

were 57 emu/g; this value was higher than that obtained by the classical ceramic method and hydrothermal method, but was close to the theoretical value for single crystals at room temperature, 72 emu/g [17–19]. The coercivity of the $BaFe_{12}O_{19}$ powders prepared from the spray solution without citric acid was 6.0 kOe. However, the coercivity of the nanosized $BaFe_{12}O_{19}$ powders prepared from the spray solution with citric acid was 4.6 kOe.

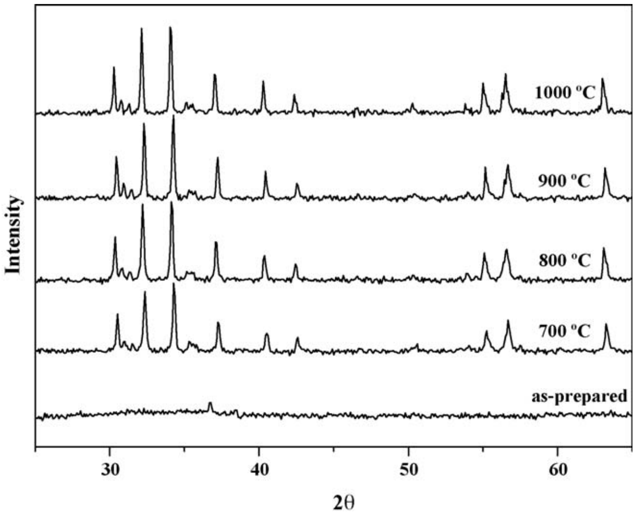


Fig. 6. X-ray diffraction patterns of $BaFe_{12}O_{19}$ powders obtained from the aqueous spray solution.

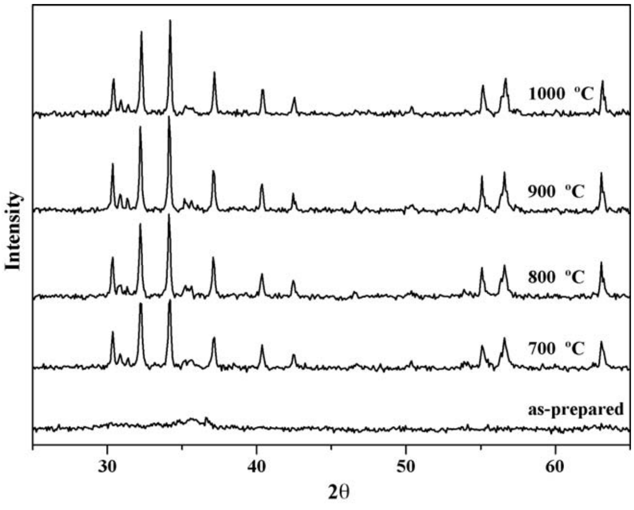
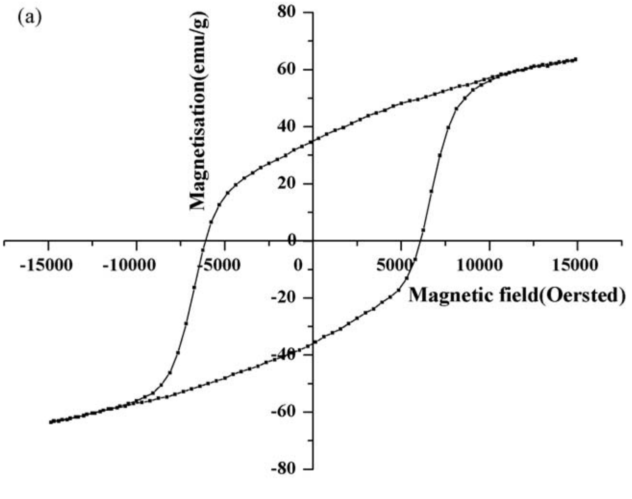
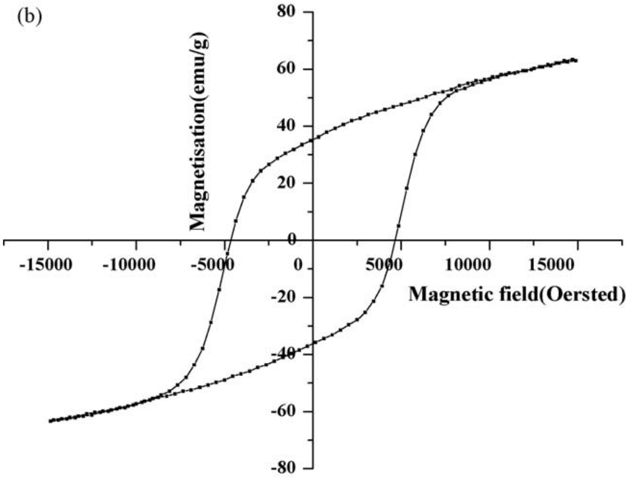


Fig. 7. X-ray diffraction patterns of $BaFe_{12}O_{19}$ powders obtained from the spray solution with CA.



Na additive



0.6 M CA

Fig. 8. Hysteresis loops of the $BaFe_{12}O_{19}$ powders post-treated at 800 °C. (a) No additive and (b) 0.6 M CA.

## 4. Conclusions

Highly crystalline nanosized $BaFe_{12}O_{19}$ were prepared by spray pyrolysis. Citric acid added to the spray solution enabled the formation of nanosized $BaFe_{12}O_{19}$ powders after post-treatment at high temperatures. The spherical shape of the precursor powders obtained from the spray solution containing citric acid was lost after post-treatment and mechanical grinding. Citric acid, which was added as an organic additive to the spray solution, affected the morphologies, mean sizes, and magnetic properties of the powders.

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