

Characteristics of barium hexaferrite nanocrystalline powders prepared by a sol-gel combustion method using inorganic agent

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Abstract Nanocrystalline particles of barium hexaferrite were synthesized by a sol-gel combustion route using nitrate-citrate gels prepared from metal nitrates and citric acid solutions under various Fe/Ba molar ratios of 10, 11 and 12. Sodium hydroxide was used as a pH-adjusting agent. The results revealed that the formation temperature of barium hexaferrite is influenced by Fe/Ba molar ratio; the Fe/Ba molar ratio of 12 is more favorable. For sample synthesized with a Fe/Ba molar ratio of 12, barium hexaferrite started to form at 800 °C and fully formed at 1000 °C. The results also showed that the coercivity of the samples decreases as the Fe/Ba molar ratio increases from 10 to 12, whilst the saturation magnetization increases.

Keywords Barium hexaferrite · Combustion · Nitrate-citrate · Sol-gel

1 Introduction

Barium hexaferrite, $\text{BaFe}_{12}\text{O}_{19}$, has been considered as a promising material for application in high-density magnetic recording media [1]. The mixed oxide ceramic method for preparing of barium hexaferrite requires a high calcining temperature (~1200 °C), which induces aggregation on the particles. Furthermore, the milling process to reduce the particle size, generally yields nonhomogeneous mixtures on a microscopic scale and induces lattice strains in the material [1]. In order to improve the material properties,

non-conventional routes such as coprecipitation [2], hydrothermal [3], sol-gel [4, 5] and citrate precursor methods [6] have also been developed.

Synthesis of barium hexaferrite by a sol-gel combustion technique using sodium hydroxide as a pH-adjusting agent is focused in the present work. The influence of Fe/Ba molar ratio on the characteristics of the products was also investigated.

2 Experimental

The starting materials were iron nitrate, barium nitrate, citric acid and sodium hydroxide, all of analytic purity. Three samples were prepared with Fe/Ba molar ratios of 10, 11 and 12, which are denoted as N1, N2 and N3, respectively. Citric acid was added into the aqueous solutions of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Ba}(\text{NO}_3)_2$ to chelate Ba^{2+} and Fe^{3+} in the solution. The molar ratio of metal nitrates to citric acid (MN/CA) was adjusted at 1:1. The mixed solution neutralized to $\text{pH} > 7$ by adding the sodium hydroxide solution. The neutralized solution was evaporated to dryness by heating at 100 °C with continuous stirring. As water evaporated, the solution became viscous and finally formed a very viscous brown gel. Increasing the temperature up to about 290 °C led to the ignition of the gel. As-burnt powder was washed and then calcined at various temperatures of 400 to 1100 °C for 1 h in air.

The thermal behavior of the samples was examined by a simultaneous differential thermal analyzer/thermal gravimetry analyzer (DTA/TGA) in air with the heating rate of 10 °C/min on the LINSEIS L70/2171 instrument. The phase identification of the samples was performed using X-ray diffraction (XRD) on a Philips PW-1730 X-ray diffractometer using Cu K_α radiation. The particle morphology examined by a Cambridge S360 scanning electron microscope (SEM).

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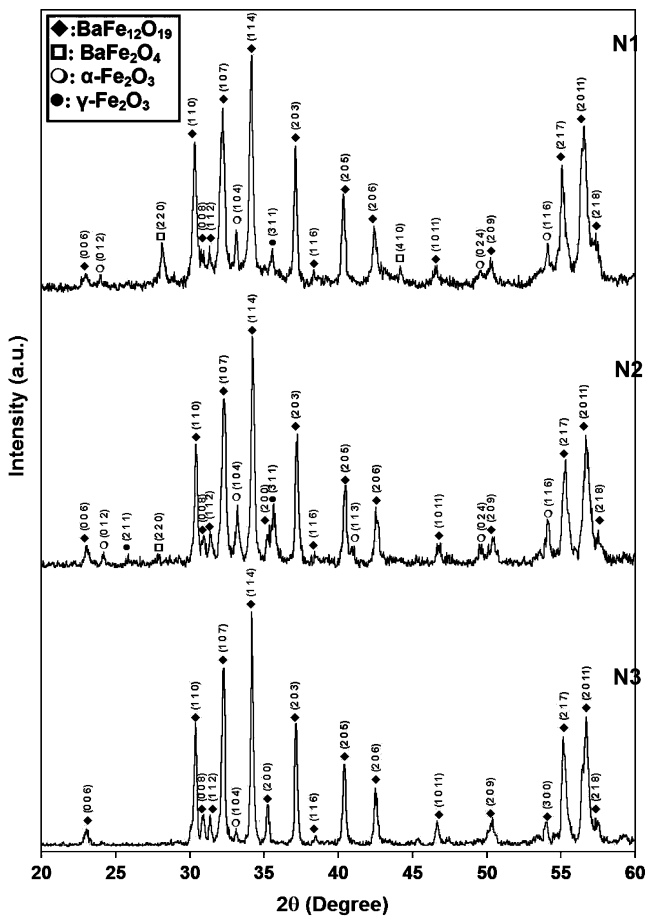


Fig. 4 XRD patterns of the samples N1, N2 and N3 all calcined at 1000 °C for 1 h

reactive Ba²⁺ ions and CO or CO₂ generated from citric acid decomposition, leads to formation of BaCO₃.

Figure 3 shows the X-ray diffraction patterns of the samples N1, N2 and N3, all calcined at 800 °C for 1 h. When the temperature is increased to 800 °C, BaCO₃ decomposes and Ba²⁺ liberated reacts with γ or α-Fe₂O₃ to form barium monoferrite (BaFe₂O₄). The reaction between barium monoferrite and iron oxide (α-Fe₂O₃ or γ-Fe₂O₃)

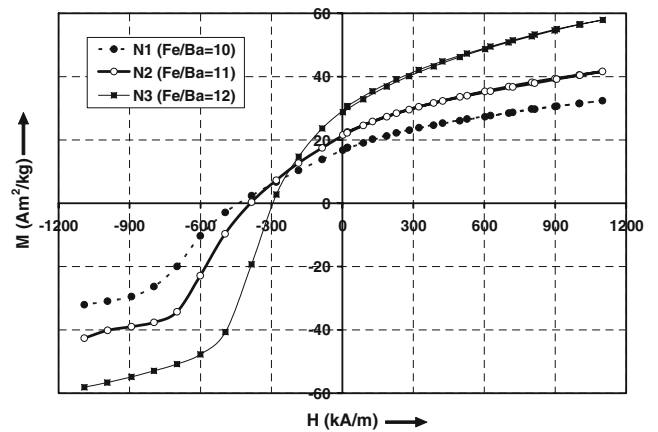


Fig. 6 Magnetization curves for samples N1, N2 and N3, all calcined at 1000 °C for 1 h

leads to formation of barium hexaferrite. The increasing of the Fe/Ba molar ratio from 10 to 11 leads to an increase on the amount of γ-Fe₂O₃ and α-Fe₂O₃ phases because of increasing of Fe³⁺ ions, whilst the amount of BaFe₂O₄ decreases due to the decrease of the Ba²⁺ ions. In sample N3, BaM is the predominant phase. It seems the Fe/Ba molar ratio of 12 is more convenient for BaM formation. The broadening of the XRD peaks in the above samples indicates that the particles are sub-micron in size.

Figure 4 shows the X-ray diffraction patterns of the samples N1, N2 and N3 all calcined at 1000 °C for 1 h. The width of the XRD peaks related to barium hexaferrite decreases as the Fe/Ba molar ratio increases, which confirms an increase in average particle size [9]. Although, the amount of barium hexaferrite increases on increasing the calcination temperature, however, a significant amount of impurities such as α-Fe₂O₃, γ-Fe₂O₃ and BaFe₂O₄ are still present in samples N1 and N2. In contrast, the sample N3 consists of almost single-phase of BaFe₁₂O₁₉ together with a small amount of α-Fe₂O₃, which was not eliminated even after calcination at 1100 °C for 1 h.

Figure 5 (a) and (b) shows the SEM micrographs of the sample N3 calcined at 1000 and 1100 °C for 1 h,

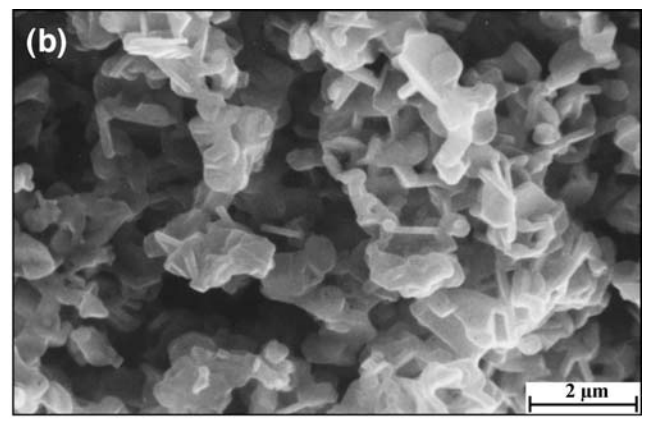
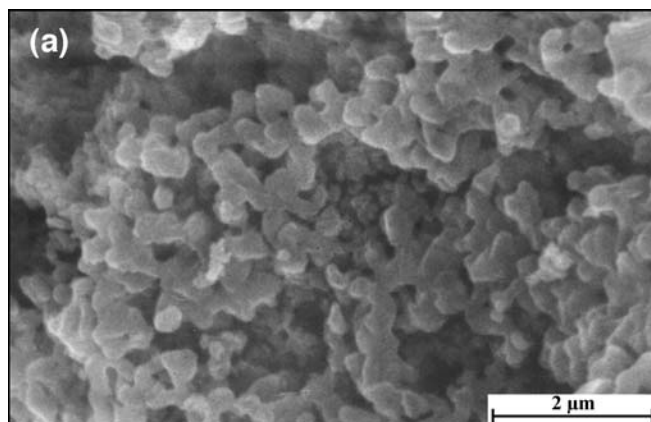


Fig. 5 SEM micrographs of the sample N3 calcined at (a) 1000 °C and (b) 1100 °C for 1 h

respectively. The sample calcined at 1000 °C consists of particles with mean particle size of 0.3 μm . It seems, the large microscopic air gaps exist between the particles decrease the diffusion rate, which hinders the particle growth. The average particle size increases from 0.3 to 0.8 μm on increasing the calcination temperature from 1000 to 1100 °C; the particles calcined at 1100 °C possess a plate-like hexagonal shape with an aspect ratio of around 8.

Figure 6 shows the magnetization curves for samples N1, N2 and N3, all calcined at 1000 °C for 1 h. The coercivity decreases as the Fe/Ba molar ratio rises from 10 to 12 probably due to the increasing of mean particles size, while the saturation magnetization increases due to the elimination of the non-magnetic phases such as $\alpha\text{-Fe}_2\text{O}_3$ and BaFe_2O_4 .

4 Conclusions

1. Nano-size particles of barium hexaferrite have been synthesized by the sol-gel combustion method using a nitrate-citrate gel in the presence of NaOH. The nitrate-citrate gel exhibits an auto-combustion behavior.
2. Formation of barium hexaferrite was found to comprise two steps: formation of monoferrite (BaFe_2O_4), fol-

lowed by reaction between monoferrite and iron oxide ($\alpha\text{-Fe}_2\text{O}_3$ or $\gamma\text{-Fe}_2\text{O}_3$) which is completed at 1100 °C.

3. Under the experimental conditions, Fe/Ba molar ratio of 12 is more favorable for formation of barium hexaferrite.

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