JOURNAL OF MATERIALS SCIENCE **39** (2004) 987–991

Effect of precursor solutions with different composition on synthesis of ultrafine $BaLa_{0.3}Fe_{11.7}O_{19}$ using sol-gel auto-combustion technique

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Hexagonal $BaLa_{0.3}Fe_{11.7}O_{19}$ ultrafine powders with a magnetoplumbite type (M-type) structure were synthesized by a sol-gel auto-combustion method. Precursor solutions with different composition were investigated to clarify the forming conditions of the ferrites. The crystal structure, grain size, form and magnetic properties were studied by means of X-ray diffraction (XRD), transmission electronic microscopy (TEM) and vibrating sample magnetometry (VSM). On the basis of analysing the effect of ammonia, citric acid and glycol on phase structure and magnetic properties, it was demonstrated that adjusting the pH value of the precursor solution with ammonia and adding an appropriate amount of citric acid and glycol are key steps in synthesis of ultrafine powders with single $BaFe_{12}O_{19}$ phase and excellent magnetic properties. In the presence of chelate agent (citric acid) and dispersant (glycol), under the conditions of pH about 7.0, nitrate/citric acid molar ratio of 1:3 and calcination temperature of 850°C (1 h), M-type $BaLa_{0.3}Fe_{11.7}O_{19}$ ultrafine powders with a particle size of about 36 nm, a specific magnetization σ s of 65.54 $A \cdot m^2/kg$ and a coercive force Hc of 433 kA/m, were obtained.

1. Introduction

Traditional barium ferrite materials are widely used as permanent magnets. Recently, more attention has been paid to them because they can also be used as perpendicular magnetic recording media with high density [1]. These applications require materials with a strict control of homogeneity, particle size and shape, and magnetic properties. The synthesis method strongly determines these characteristics.

During the last few decades, people have made great efforts to prepare ferrite powders with high performance. On the one hand, people managed to reduce the particle size of the powders by various techniques such as chemical co-precipitation [2], hydrothermal method [3], hydrolysis of metal-organic complexes [4], glass crystallization [5], microemulsion method [6], cryochemical method [7], aerosol synthesis [8] and sol-gel technique [9]. On the other hand, people tried to use microelement doping [10].

In our work, both the synthesis method and microelement doping were considered to prepare high performance powder materials. Considering their special properties and abundance in China, rare earths were used as doping elements in this work so as to improve the magnetic properties of barium ferrite and widen their application market.

We report in this paper an analysis of the influence of solutions' composition on structure, morphology and magnetic properties of $BaLa_{0.3}Fe_{11.7}O_{19}$ particles prepared using the sol-gel auto-combustion technique.

2. Experimental

According to the composition of the ferrite $BaLa_{0.3}Fe_{11.7}O_{19}$, stoichiometric amount of ferric nitrate, barium nitrate and lanthanum nitrate which was prepared by the reaction between La_2O_3 and HNO_3, was dissolved in distilled water with or without subsequent addition of citric acid (the molar ratio of nitrate/citrate = 1/3) and/or glycol (the molar ratio of citrate/glycol = 1/3). The initial pH of the solution was adjusted with ammonia solution addition. The obtained solution was slowly evaporated until a viscous liquid was formed and it was evaporated in vacuum to form the dry gel. The gel was further spontaneously ignited by heating in the air followed by self-propagating combustion for the purpose of decomposing the organic precursor to form dendritic fluffy powders [11]. Finally, the powders were calcined at 850°C for 1 h.

The sol-gel auto-combustion technique in this work offers the following advantages: the intimate mixing of the starting materials on an ionic level, the convenient adding and control of chemical agents, the lower annealing temperature in the crystallization, the small particles and narrow size distribution, and the low production cost.

Chemical composition and pH values of precursor solutions for preparing six samples are listed in Table I.

The synthesized powders were characterized using XRD and TEM. The specific magnetization, σ_s, and coercive force, Hc of unoriented assemblies of the prepared powders were measured by means of VSM at a maximum applied field of 1107 kA/m at room temperature. The average size of crystallite ($D^{\#}$) was deduced from the width of XRD maxima by applying the classical Scherrer equation.

TABLE I Chemical composition of different solutions

Samples	Chemical agents	pH
A	Citric acid + glycol	1.10
B	Citric acid + glycol + $NH_3 \cdot H_2O$	6.96
C	Citric acid	1.04
D	Glycol	1.74
E	Citric acid + $NH_3 \cdot H_2O$	6.96

TABLE II Crystal phases of five samples after combustion

Samples	Crystal phase
A_{comb}	γ-Fe_2O_3 + α-Fe_2O_3
B_{comb}	γ-Fe_2O_3
C_{comb}	γ-Fe_2O_3 + α-Fe_2O_3
D_{comb}	γ-Fe_2O_3 + α-Fe_2O_3
E_{comb}	γ-Fe_2O_3

3. Results and discussion

3.1. Experimental results

The crystal phases of five samples after combustion (A_{comb}–E_{comb}) are shown in Table II. In all samples, the γ-Fe_2O_3 was the sole phase or main phase. No detectable α-Fe_2O_3 was found in samples B and E. Only small amounts ofα-Fe_2O_3 existed in samples A, C and D.

After combustion the powders were further annealed at 850°C for 1 h using a heating rate of 10°C/min. The crystal structure and magnetic properties of samples A_{850}–E_{850} are shown in Table III. TEM of these samples is shown in Fig. 1.

In samples B_{850} and E_{850}, the $BaFe_{12}O_{19}$ was the sole phase. No detectable α-Fe_2O_3 was found in them. However, small amounts of α-Fe_2O_3 existed in samples A_{850} and C_{850} besides $BaFe_{12}O_{19}$. Especially, in sample D_{850}, the main phase is the α-Fe_2O_3, not the $BaFe_{12}O_{19}$.

3.2. Discussion

3.2.1. The effect of ammonia on phase structure

After combustion, the phases of γ-Fe_2O_3 and α-Fe_2O_3 are obtained in sample A_{comb} (pH = 1.10), whereas in sample B_{comb} (pH = 6.96), only γ-Fe_2O_3 phase is obtained, and no α-Fe_2O_3 phase is detectable. The same phenomenon could be observed by comparing sample C_{comb} with sample E_{comb}. Therefore, the presence of ammonia in the precursor solution strongly determines the phase structure of the samples in the intermediate state before calcination.

On the basis of the results in Tables II and III, it can be observed that if α-Fe_2O_3 exists in the intermediate state, the final sample (A_{850}, C_{850}) after annealing contain a mixture of $BaFe_{12}O_{19}$ and α-Fe_2O_3 phases, whereas sample B_{850} and E_{850} are completely single $BaFe_{12}O_{19}$ phase because the intermediate phase is γ-Fe_2O_3 only. This indicates that the conversion of α-Fe_2O_3 in the intermediate state into the $BaFe_{12}O_{19}$ is quite difficult.

As we all know, γ-Fe_2O_3 is a cubic spinel, whose chemical formula is $Fe\,[Fe_{5/3}\square_{1/3}]O_4$, where $\square$ stands for a cation hole [1]. Its structure is similar to that of "S" block in Ba-ferrite, thus γ-Fe_2O_3 can be easily converted into $BaFe_{12}O_{19}$ phase. whereas α-Fe_2O_3 is $FeTiO_3$-type structure which belongs to the trigonal crystal system. Its crystal cell is orthorhombic hexahedron which is difficult to transform to $BaFe_{12}O_{19}$ phase. Therefore, the crystal structure of intermediate Fe_2O_3 plays an important role in the formation of $BaFe_{12}O_{19}$ phase.

TABLE III Results of XRD, VSM and average size of crystallites

Samples	Crystal phase	б$_\mathrm{s}$ (A $\cdot$ m^2/kg)	б$_\mathrm{r}$ (A $\cdot$ m^2/kg)	Hc (kA/m)	$D^{\#}$ (nm)
A_{850}	$BaFe_{12}O_{19} + \alpha\text{-}Fe_2O_3$	50.71	26.89	371	60
B_{850}	$BaFe_{12}O_{19}$	65.54	35.42	433	36
C_{850}	$BaFe_{12}O_{19} + \alpha\text{-}Fe_2O_3$	32.06	17.28	372	74
D_{850}	$\alpha\text{-}Fe_2O_3 + BaFe_{12}O_{19}$	24.32	12.24	351	55
E_{850}	$BaFe_{12}O_{19}$	62.34	33.08	405	42

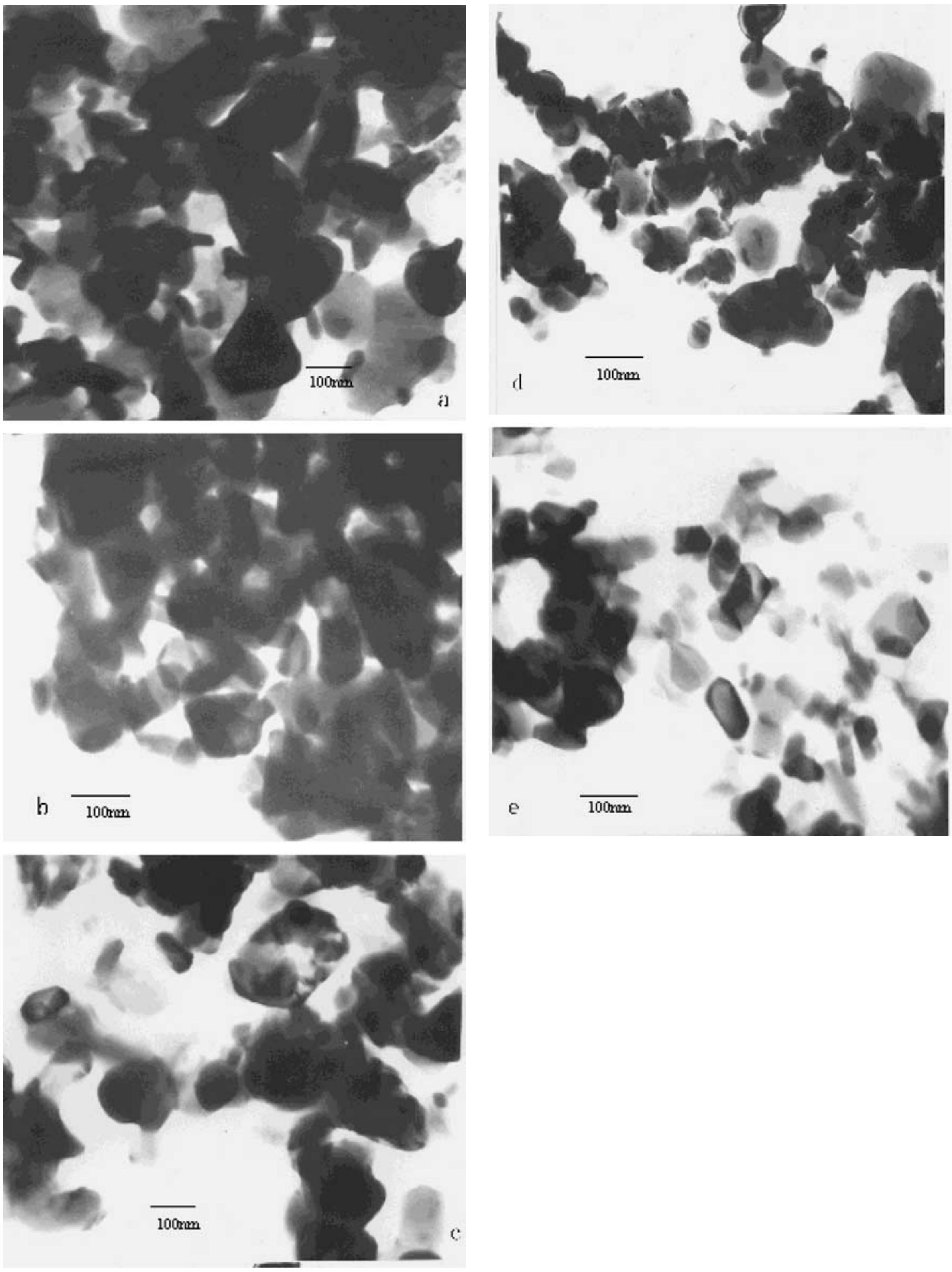

Figure 1 TEM of samples with different composition of solutions: (a) A_{850}, (b) B_{850}, (c) C_{850}, (d) D_{850}, and (e) E_{850}.

3.2.2. *The effect of ammonia on magnetic properties*

The magnetic properties of samples are also listed in Table III. As we know, their magnetism is mainly from the $BaFe_{12}O_{19}$, hard magnetic crystal phase, not from the α-Fe_2O_3, a non-magnetic phase. The results of VSM showed that the specific magnetization and coercive force of sample B_{850} and E_{850} are larger than those of sample A_{850} and C_{850}, which is in agreement with the results of XRD.

In addition, the homogeneity and the average size of crystallites also determine the magnetic properties. It can be seen from Fig. 1 that the samples A_{850} and C_{850} consist of two kinds of particles showing different morphologies, i.e., spherical particles of a diameter ranging from 20 to 30 nm and hexagonal platelets with a size distribution in the range 30–150 nm. In contrast, the particles of samples B_{850} and E_{850} are homogeneous hexagonal platelet crystals only, with a narrower size distribution and perfect crystal phase. The average size of crystallite deduced by applying the classical Scherrer equation and the results detected from TEM, showed that the average size of crystallite in samples B_{850} and E_{850} are 36 nm and 42 nm respectively, which are much smaller than that in samples A_{850} and C_{850}. Therefore, the fact that the magnetic properties of samples B_{850} and E_{850} are better than those of A_{850} and C_{850} certainly indicates the presence of a proportion of large multi-domain grains and fine superparamagnetic particles which can reduce the overall coercive force by domain nucleation.

In summary, adjusting the pH value of precursor solution by adding ammonia is a key step in synthesis of ultrafine powders with single $BaFe_{12}O_{19}$ phase and excellent magnetic properties using the sol-gel auto-combustion technique.

3.2.3. *The effect of citric acid*

Whether citric acid is present or not is the difference between precursor solutions A and D. By comparing the results of sample A_{850} with D_{850} in Table III, it can be concluded that whether citric acid is present in the precursor solution has an effect on both the phase structure and the magnetic properties. After calcination, the $BaFe_{12}O_{19}$ phase is the main phase in A_{850}, whereas the main phase in sample D_{850} is α-Fe_2O_3. As magnetic properties are governed by the phase composition, the specific magnetization and coercive force of sample D_{850} are much smaller than those of A_{850}. Therefore, citric acid acting as chelate agent is indispensable.

With increasing amount of citric acid, the magnetic properties improve greatly. The magnetic properties of powders with various amounts of citric acid are listed in Table IV.

It is said that when there is excessive citric acid in the solution, citric acid plays roles of not only chelate agent but also dispersant. Thus, the particles could be prevented from agglomerating in the later processes [12].

3.2.4. *The effect of dispersant (glycol)*

It can be seen from Table I that whether glycol is present or not is the difference between precursor solution B and E. By comparing the results of sample B_{850} with E_{850} in Table III, it can be concluded that whether glycol is present in precursor solution has no effect on the crystal structure but has an important effect on the particle size and magnetic properties. After calcination, the single $BaFe_{12}O_{19}$ phase is obtained in both sample B_{850} and E_{850}. However, the magnetic properties of sample B_{850} are better than those of E_{850}. For example, the coercive force of B_{850} is 433 kA/m, whereas E_{850} is 405 kA/m. And the average size of crystallite in sample B_{850} is smaller than that in sample E_{850}. The same phenomenon could be observed by comparing sample A_{850} and C_{850}. Therefore, the adding of glycol is necessary due to its characteristics of easy polymerization.

TABLE IV Magnetic properties of powders at various amount of citric acid

	Magnetic properties		
n (Citrate): *n* (Nitrate)	б$_s$ (A · m^2/kg)	б$_r$ (A · m^2/kg)	Hc (kA/m)
1:1	55.90	29.98	365
1.5:1	61.13	33.6	422
3:1	65.54	35.42	433

Glycol's molecular formula is $OH{-}CH_2{-}CH_2{-}OH$. It can act as both dispersant and assistant chelate agent. With the addition of glycol, the precursor solution consists of long chains of organic molecules. It can strengthen the complexing of barium ion and citric acid, quicken Brownian Motion, enhance the diffusivity and stabilize the dynamics, leading to small particles.

4. Conclusions

Precursor solutions with different composition were investigated to clarify the forming conditions of ferrites. On the basis of analysing the effect of ammonia, citric acid and glycol on phase structure and properties, the following conclusions were reached:

(1) Whether ammonia solution is present in the precursor solution strongly determines the phase structure of the samples in the intermediate state before calcination.

(2) The crystal structure of intermediate Fe_2O_3 plays an important role in the formation of $BaFe_{12}O_{19}$ phase. If α-Fe_2O_3 exists in the intermediate state, the final sample after annealing is a mixture of $BaFe_{12}O_{19}$ and α-Fe_2O_3 phases, not completely single $BaFe_{12}O_{19}$ phase because the conversion of α-Fe_2O_3 in the intermediate state into the $BaFe_{12}O_{19}$ is quite difficult.

(3) The phase structure, the homogeneity and the average size of crystallites determine the magnetic properties.

(4) With an increase of the amount of citric acid, the magnetic properties improve greatly.

(5) Whether glycol is present in the precursor solution has no effect on the crystal structure but has important effect on the particle size and magnetic properties.

In summary, the sol-gel auto-combustion technique is an effective method to prepare homogeneous ultrafine $BaLa_{0.3}Fe_{11.7}O_{19}$ powders. Adjusting the pH value of precursor solution with ammonia and adding an appropriate amount of citric acid and glycol are key steps in synthesis of ultrafine powders with single $BaFe_{12}O_{19}$ phase and excellent magnetic properties. Only with the pH of approximately 7.0 and in the simultaneous presence of citric acid and glycol, can the formation of α-Fe_2O_3 phase in the intermediate state be prevented, and thus ultrafine pure $BaLa_{0.3}Fe_{11.7}O_{19}$ powders be obtained at relatively low temperature(in the case of 850°C). The final $BaLa_{0.3}Fe_{11.7}O_{19}$ powder with an average crystallite size of 36 nm prepared under the optimum conditions exhibits a specific magnetization б s of 65.54 $A \cdot m^2/kg$ and a coercive force Hc of 433 kA/m, close to the theoretical expected values [1] and greatly improved compared with $BaFe_{12}O_9$ powders (without the doping of rare earth La) prepared by the same technique.

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Received 2 December 2002
and accepted 7 July 2003