

[Article ID] 1003- 6326(2001) 03- 0447- 04

## Synthesis and characterization of La doped M-type hexagonal barium ferrite fine powders<sup>①</sup>

LI Hong-gui(李洪桂), GUO Ru-qian(郭睿倩), SUN Pei-mei(孙培梅),

LI Yun-jiao(李运姣), ZHAO Zhong-wei(赵中伟),

LIU Mao-sheng(刘茂盛), SU Peng-tuan(苏鹏转)

(Department of Metallurgy Science and Engineering, Central South University,  
Changsha 410083, P. R. China)

**[Abstract]** The hexagonal  $\text{BaLa}_x\text{Fe}_{12-x}\text{O}_{19}$  fine powders with M-type structure were synthesized by sol-gel method. The pH of the solution, the molar ratio of nitrate to citric acid and the calcination temperature were investigated to clarify the forming conditions of the ferrites. The crystal structure, grain size, form and magnetic properties were studied by means of XRD, SEM and vibrating sample magnetometer. It is concluded that at pH of 7.0 or so, molar ratio of nitrate to citric acid of 1/3 and calcination temperature of 850 °C (1 h), 1 000 °C, M-type  $\text{BaLa}_x\text{Fe}_{12-x}\text{O}_{19}$  fine powders with a particle size of less than 300 nm was obtained.

**[Key words]** sol-gel method; rare earth; permanent magnetic ferrite; citrate

**[CLC number]** TF 123

**[Document code]** A

### 1 INTRODUCTION

Permanent barium ferrite materials are widely used. Recently, people have paid more attention to them because they can also be used as perpendicular magnetic recording media with high density in new magnetic recording field<sup>[1]</sup> and materials acting as concealment in arms industry<sup>[2]</sup>. Thus the study on the synthesis of magnetoplumbite-type barium ferrite is considerably important to the electronic and magnetic materials industry.

During the last few decades, people have made great efforts to prepare barium ferrite powders with high performance. On one hand, people managed to reduce the particle size of the powders by various techniques such as chemical co-precipitation<sup>[3, 4]</sup>, hydrothermal method<sup>[5]</sup>, hydrolysis of metal-organic complexes<sup>[6]</sup>, glass crystallization<sup>[7]</sup> and microemulsion method<sup>[8]</sup>. On the other hand, people committed themselves to microelement doping.

In our work, both synthesis method and microelement doping were considered to prepare high performance powder materials, and sol-gel method was combined with self-propagating high-temperature synthesis<sup>[9]</sup> to develop sol-gel auto-combustion high-temperature synthesis. On the other hand, considering that rare earths are abundance elements in our country and the study on synthesis of a series of rare earths doped ferrite by this method has never been reported, they were used as doping elements in our study so as to improve the properties of permanent magnetic ferrite and widen their application market.

Here the hexagonal  $\text{BaRE}_x\text{Fe}_{12-x}\text{O}_{19}$  fine pow-

ders with M-type structure are synthesized by sol-gel auto-combustion high-temperature synthesis method. Synthesis conditions of La, Nd, Gd, Sm doped hexagonal barium ferrite fine powders and effect of their doping amount on magnetic properties of barium ferrite are studied.

### 2 EXPERIMENTAL

Ferric nitrate, barium nitrate and lanthanum oxide and citric acid of AR grade were used as raw materials. According to the preconcerted composition of the ferrite  $\text{BaLa}_x\text{Fe}_{12-x}\text{O}_{19}$  ( $x = 0 \sim 1$ ), stoichiometric amount of ferric nitrate, barium nitrate and lanthanum nitrate which was prepared by the reaction between  $\text{La}_2\text{O}_3$  and  $\text{HNO}_3$ , was dissolved in distilled water with subsequent addition of different amount of citric acid to control the molar ratio of nitrate to citrate at about 1/3, 2/3 and 1. And then the initiative pH of solution was adjusted by ammonia solution. The obtained solution was slowly evaporated until a viscous liquid was formed and it was further evaporated at 135 °C in vacuum to form the dry gel, which was further ignited in the air followed by self-propagating combustion for the purpose of decomposing the organic precursor to form dendritic fluffy powders. Finally, the powders were calcined at different temperatures.

The behavior of the dried gels in combustion and calcination process were studied by DTA-TG. The synthesized powders were characterized in terms of XRD and SEM. The specific magnetization,  $\sigma_s$ , and coercive force,  $H_c$  of unoriented assemblies of the prepared powders were measured by means of vibrat-

ing sample magnetometer (VSM) at a maximum applied field of 1107 kA/m at room temperature.

### 3 RESULTS AND DISCUSSION

#### 3.1 Effect of pH

Two samples with the composition of  $\text{BaLa}_{0.3}\text{Fe}_{11.7}\text{O}_{19}$  were prepared by the above procedure from two precursor solutions.

Sample *a*: the pH of the precursor solution was adjusted to 7.28 by the adding of ammonia solution.

Sample *b*: without adding ammonia solution, so the PH of the precursor solution is 0.5, other conditions are the same as sample *a*.

The comparison of sample *a* and sample *b* in terms of XRD is shown in Fig. 1.

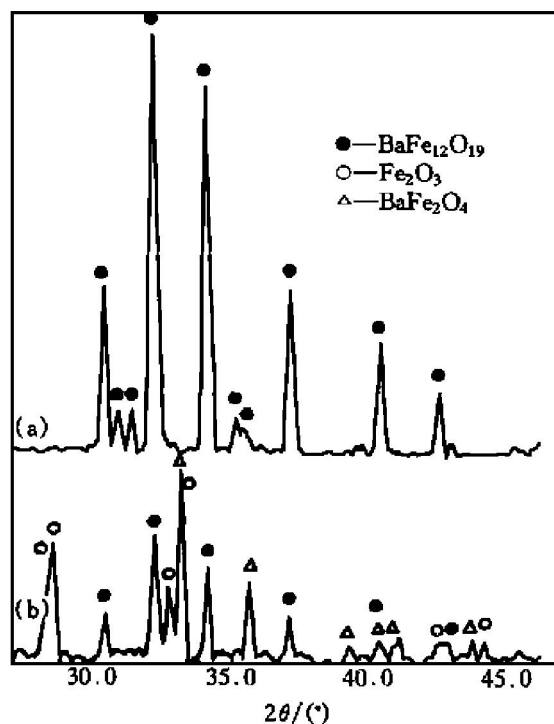


Fig. 1 X-ray diffraction patterns of  $\text{BaLa}_{0.3}\text{Fe}_{11.7}\text{O}_{19}$  formed by sol-gel method at various pH of solution  
(a) —pH= 7.28; (b) —pH= 0.5

As shown in Fig. 1, sample *a* formed at pH of 7.28 is recognized to be magnetoplumbite barium ferrite, but sample *b* formed at pH of 0.5 contains  $\text{Fe}_2\text{O}_3$  and  $\text{BaFe}_2\text{O}_4$  besides magnetoplumbite barium ferrite. Therefore, pH has important effect on the structure of  $\text{La-Ba}$  ferrite fine powders.

#### 3.2 Effect of molar ratio of nitrate to citric acid

##### 3.2.1 DTA-TG of gel

According to the molecular formula  $\text{BaLa}_{0.3}\text{Fe}_{11.7}\text{O}_{19}$ , three gels were prepared by the above procedure from the precursor solution of pH= 7.0 or so.

Gel *a*: molar ratio of nitrate to citric acid= 1: 1;

Gel *b*: molar ratio of nitrate to citric acid= 1: 1.5;

Gel *c*: molar ratio of nitrate to citric acid= 1: 3.

It was found that the gel transformed from the aqueous solution of metal nitrate and citric acid has the characteristics of self-propagating combustion. That is, once the gel was ignited at one side, the combustion would propagate ahead to the other side smoothly at very fast speed, complete combustion to form fluffy powders. Fig. 2 shows DTA-TG curves of the three gels.

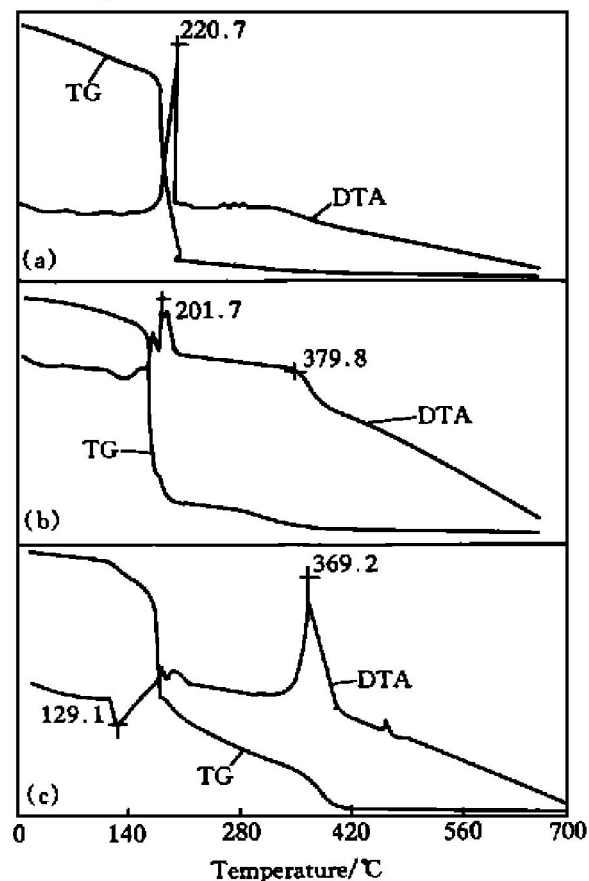
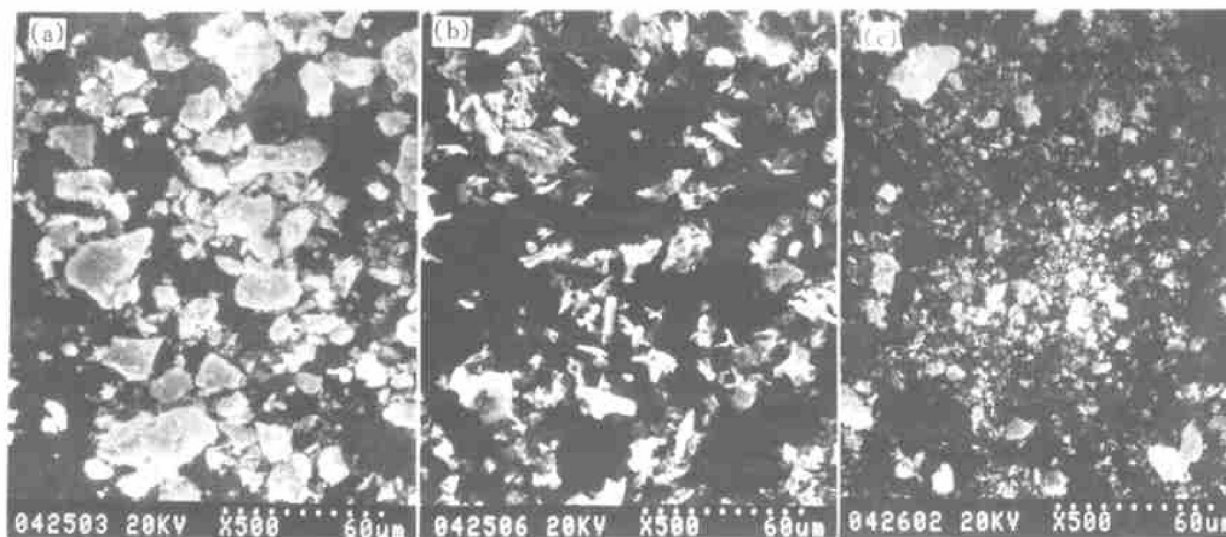


Fig. 2 DTA-TG curves of three gels at various amounts of citric acid  
(molar ratio: (a) —1: 1; (b) —1: 1.5; (c) —1: 3)

It can be concluded from Fig. 2 that when the ratio of nitrate to citric acid is 1: 1, there exists only one exothermic peak at the temperature of 220 °C with the mass loss of 11% in DTA-TG curve (a), which correspond to the self-propagating combustion of the sample. With the increase of the amount of citric acid, there is another peak at about 375 °C in DTA-TG curves (b) and (c), which corresponded to the decomposition of excessive citric acid<sup>[10]</sup>. In addition, the endothermic peak at 129 °C in DTA-TG curve (c) is in correspondence to the melting of gel, which is in agreement with the experimental phenomena.

##### 3.2.2 Microstructures of powders

The above three gels were ignited in the air respectively followed by combustion and grinding, and then calcined at 850 °C(1 h) and 1 000 °C. SEM of ferrite powders at various citric acid amount are shown in Fig. 3.



**Fig. 3** SEM of ferrite powders at various molar ratios of nitrate to citric acid  
(molar ratio: (a) —1: 1; (b) —1: 1.5; (c) —1: 3)

As shown in Fig. 3, the more the amount of citric acid is, the smaller the size of the particle is, and at a molar ratio of 1: 3, the fine powders with a particle size of less than 300 nm could be prepared. The effect of molar ratio of nitrate to citric acid on the particle size can be explained as: when there has 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 glomerating in the later processes.

### 3.3 Effect of calcination temperature

The above gel *c* was ignited in the air followed by combustion and grinding, and then the produced powders were calcined respectively at the temperature of 450 °C(1 h), 550 °C(1 h), 650 °C(1 h), 750 °C(1 h), 850 °C(1 h) and 850 °C(1 h), 1 000 °C. XRD patterns of powders calcined at different temperatures are shown in Fig. 4.

It is concluded from Fig. 4 that the samples calcined at lower temperature such as 450 °C and 550 °C are recognized to be ferric oxide. Besides ferric oxide, there occurred  $\text{BaFe}_2\text{O}_4$  in the sample calcined at 650 °C. Most of the product calcined at 750 °C was magnetoplumbite barium ferrite with only a little  $\text{Fe}_2\text{O}_3$ . Only when the temperature was increased to 850 °C or more than 850 °C, could the powders be recognized to be completely magnetoplumbite barium ferrite.

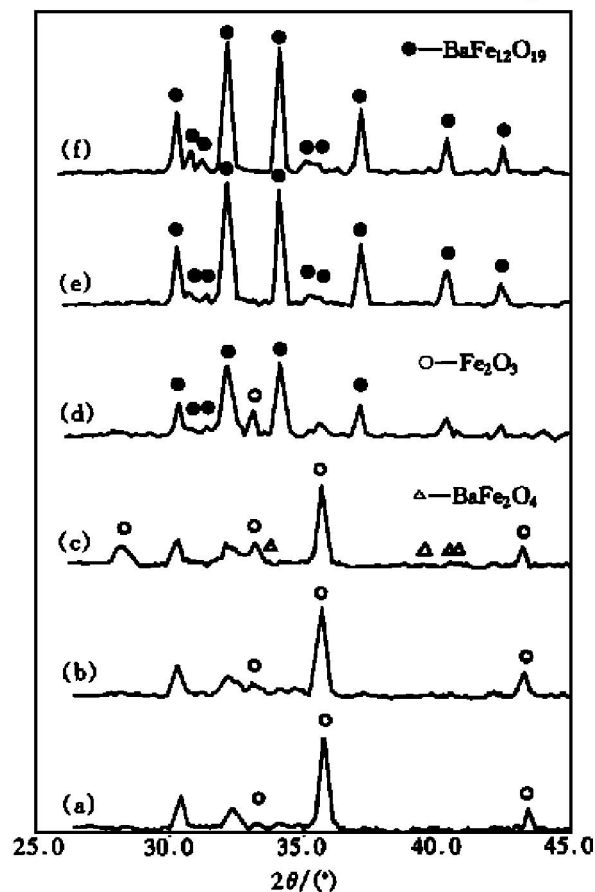
### 3.4 Magnetic properties

The effect of the amount of doped lanthanum on magnetic properties of barium ferrite fine powders are shown in Table 1.

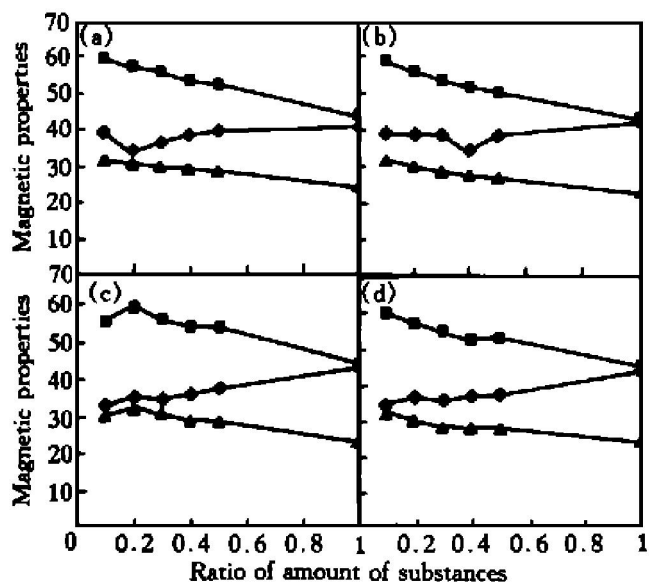
As shown in Table 1, with the increase of the amount of La, both the specific saturation magnetization(  $\sigma_s$ ) and the specific remanent magnetization(  $\sigma_r$ ) decrease gradually, whereas there exists a nadir of cor-

ercive force(  $H_c$ ) under the condition of  $x = 0.2$ , as shown in Fig. 5.

The study on Nd, Sm, Gd doped hexagonal barium ferrite shows that there is a similar regularity



**Fig. 4** XRD patterns of ferrite powders at different calcination temperatures  
(a) —450 °C; (b) —550 °C;  
(c) —650 °C; (d) —750 °C; (e) —850 °C;  
(f) —850 °C(1 h), 1 000 °C



**Fig. 5** Effect of amount of La, Sm, Gd and Nd on magnetic properties

◆— $H_c / (10^4 \text{ A} \cdot \text{m}^{-1})$ ; ■— $\sigma_s / (\text{A} \cdot \text{m}^2 \cdot \text{kg}^{-1})$ ;  
▲— $\sigma_r / (\text{A} \cdot \text{m}^2 \cdot \text{kg}^{-1})$

(a) — $n(\text{La})$ :  $n(\text{Ba})$ ; (b) — $n(\text{Sm})$ :  $n(\text{Ba})$ ;

(c) — $n(\text{Gd})$ :  $n(\text{Ba})$ ; (d) — $n(\text{Nd})$ :  $n(\text{Ba})$

**Table 1** Magnetic properties of  $\text{BaLa}_x\text{Fe}_{12-x}\text{O}_{19}$

Sample	$H_c$ $/(10^4 \text{ A} \cdot \text{m}^{-1})$	$\sigma_s$ $/( \text{A} \cdot \text{m}^2 \cdot \text{kg}^{-1} )$	$\sigma_r$ $/( \text{A} \cdot \text{m}^2 \cdot \text{kg}^{-1} )$
$x = 0.0$	39.12	59.87	32.55
$x = 0.1$	39.70	59.57	31.87
$x = 0.2$	34.48	57.17	30.92
$x = 0.3$	36.53	55.90	29.98
$x = 0.4$	38.60	53.39	29.44
$x = 0.5$	39.93	52.61	28.81
$x = 1.0$	41.05	44.05	24.66

in magnetic properties of these powders, as also shown in Fig. 5.

#### 4 CONCLUSIONS

1) The hexagonal  $\text{BaLa}_x\text{Fe}_{12-x}\text{O}_{19}$  fine powders with M-type structure were synthesized by sol-gel self-propagating high-temperature synthesis technique. pH of the solution and the calcination temperature have important effect on powders crystal phase. It was concluded that the products prepared at pH of

about 7.0 and at 850 °C (1 h), 1 000 °C were recognized to be only magnetoplumbite barium ferrite.

2) The size of the particles depends on the amount of citric acid, the more the amount of citric acid is, the smaller the size of the particles will be; and at a molar ratio of 1: 3, the fine powders with a particle size of less than 300nm could be prepared.

3) With the increase of the amount of  $\text{La}^{3+}$ , both the specific saturation magnetization ( $\sigma_s$ ) and the specific remanent magnetization ( $\sigma_r$ ) decrease gradually, whereas there exists a nadir of coercive force ( $H_c$ ) at the condition of  $x = 0.2$ . And there is a similar regularity in magnetic properties of Nd, Sm, Gd doped hexagonal barium ferrite powders.

#### [ REFERENCES ]

- [ 1 ] TIAN Yur-lin. Preparation and magnetic properties of oriented barium ferrite ultrafine powders [ J ]. Bulletin Society, 1989, 8(1): 21– 29.
- [ 2 ] FENG Quarryuan, REN Lang. Polycrystalline hexaferrites for millimeter wave applications [ J ]. Journal of Functional Materials, 2000, 31(1): 48– 49.
- [ 3 ] Pankov V V, Pernet M, Germi P, et al. Fine hexaferrite particles for perpendicular recording prepared by the coprecipitation method in the presence of an inert component [ J ]. J Magn Magn Mat, 1993, 120: 69– 72.
- [ 4 ] SHAO Yuarrzhi, ZHANG Tie-li, ZHOU Ruozhen, et al. Preparation and magnetic properties of  $\text{BaFe}_{11-x-y}\text{Co}_{0.5}\text{Ti}_{10.5}\text{Ni}_x\text{Zn}_y\text{O}_{19}$  [ J ]. Journal of Functional Materials, 1992, 23(4): 230– 233.
- [ 5 ] Lin C H, Shih Z W, Chin T S, et al. Hydrothermal processing to produce magnetic particulates [ J ]. IEEE Transactions on Magnetics, 1990, 26(1): 15– 17.
- [ 6 ] Haneda K, Miyakawa C, Goto K. Preparation small particles of  $\text{SrFe}_{12}\text{O}_{19}$  with high coercivity by hydrolysis of metal-organic complexes [ J ]. IEEE Trans Magn, 1987, MAG-23: 3134– 3136.
- [ 7 ] Oda K, Yoshio T, O-Oka K. Magnetic properties of  $\text{SrFe}_{12}\text{O}_{19}$  particles prepared by the glass-ceramic method [ J ]. J Mater Sci Let, 1984, 3(11): 1007– 1010.
- [ 8 ] Pillai Vinod, Kumar Promod, Shah D O. Magnetic properties of barium ferrite synthesized using a microemulsion mediated process [ J ]. J Magn Magn Mat, 1992, 116: L299.
- [ 9 ] ZHANG Yarr-an, HE Jircheng. Development of study on self-propagating high-temperature synthesis [ J ]. The Chinese Journal of Nonferrous Metals, ( in Chinese ), 1998, 8(Suppl. 2): 272.
- [ 10 ] YUE Zhen-xing, ZHOU Ji, ZHANG Hong-guo, et al. Synthesis of nanometer NiZn ferrite powders by sol-gel auto-combustion [ J ]. Chinese Journal of Material Research, ( in Chinese ), 1999, 13(5): 484– 486.

( Edited by LONG Huai-zhong )