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Influences of preheat treatment on the anisotropy and particle size of $BaTiCoFe_{10}O_{19}$ powders

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Ultrafine substituted M-type barium ferrite $BaTiCoFe_{10}O_{19}$ powders were synthesized successfully by sol-gel method**.** The hydroxide precursor particles were formed in gel solution containing ethanol and water at a ratio of 1:1 and NaOH as co-precipitation agent. The effects of preheat treatments on formation and anisotropy of $BaTiCoFe_{10}O_{19}$ powders were studied using XRD and SEM. The XRD analysis indicated single phase $BaTiCoFe_{10}O_{19}$ powders were formed. The average particle sizes of the powders were about 40nm. Calculation of c/a value with XRD data indicated that the Ti-Co-substitution and preheat treat changed drastically atomic lattice anisotropy of hexaferrite powders. The average c/a ratio increased from 3.9347 for $BaFe_{12}O_{19}$ powders to 3.9415 for no preheat treat and 3.9392 and 3.9432 for preheat treat for 1h at 300°C and 400°C respectively. SEM analyses revealed that the particles had platelike morphology and the aspect ratio in morphology of the powders non-preheated and preheated at 400°C were larger than that of powders preheated at 300°C.

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Keyword: Sol-gel method, Preheat treatment, $BaTiCoFe_{10}O_{19}$, powder, Magnetic anisotropy, c/a ratio

1. Introduction

Barium hexaferrite exhibits a high saturation magnetization and a high coercivity and a high magnetic permeability and a large gyromagnetic effect and a relatively high magnetocrystalline anisotropy field and hexa-platelike morphology and chemical stability and corrosion resistivity that can be used for many challenging applications, such as for high-density type perpendicular recording media[1] and microwave materials and microwave absorption materials. Hexaferrites are especially best microwave absorption materials among various ferrites. Some cation substitutions can further change the anisotropy energy. Ti-Co-substituted M-type Ba-ferrites $Ba(TiCo)_xFe_{10-2x}O_{19}$ are of a higher magnetic anisotropy and have been explored as microwave materials and microwave absorption materials[2-5]. The microwave properties of Ti-Co-substituted barium ferrite are largely dependent on the characters multidomain ferrite powders except for Ti-Co-substitution rate. Many processing routes have been devised for the preparation of a barium ferrite powder with refined particle size, narrow particle-size distribution, minimal particle agglomeration, and high crystallinity, including hydrothermal process[6], microemulsion technique[7] et al. The characters of powders can be influenced by the technological factors in processes of preparing the ferrites with these processing routes, such as, molten-salt method was effective for decreasing the particle size and the agglomeration of powders, preheat treatment have been verified to be effective in decreasing the particle size of powders, the magnetic structure in doped Ba-hexaferrites changed drastically when the calcining temperature was altered[5]. Preheat treatment also can influences the formation process of $Ba(TiCo)_xFe_{12-2x}O_{19}$ powders and further influences the anisotropy of the powders. However this effect has not be reported previously.

Sol-gel method have advantages of low cost and simple technological process and is an useful method to prepare ultrafine Co-Ti-substituted Ba-ferrite powders with single-domain perfect crystallography, narrow size distribution and excellent magnetic properties and perfect absorbing ability. The objectives of this paper are to present effects of preheat treatment on the anisotropy and particle size and formation of the Co-Ti-substituted M-type Ba-ferrite powders prepared by sol-gel method.

2. Experimental procedure

(1) Preparation of hydroxide Precursor

The ferric chloride hexahydrate and barium chloride dihydrate and cobalt chlorite hexahydrate and titanium propoxide at a composition of $BaTiCoFe_{10}O_{19}$ were dissolved in the solution containing ethanol and water at ratio of 1:1 and stabilized with little acetylaccetone to prevent the titanium propoxide from hydrolyzing and stirred for 0.5h. In the solution, the molar concentration were 0.02M for Ba^{2+}, Co^{2+}, and Ti^{2+} cation and was 0.2M for Fe^{3+} cation, respectively. Then, sodium hydroxide aqueous solution was dropwisely slowly added into the resultant solutions at room temperature with constant stirring condition until pH>9. After coprecipitation was completed, the precipitate slurry was filtrated and washed with anhydrous ethanol until pH~7 and dried for 4-10h at 100°C.

(2) Heat treatment and powder characterization

The two portions of as-dried precursors were preheated at 300°C and 400°C for 1h respectively. As-dried precursors and as-preheated precursors were heated at heating rate of 25°C/min and calcined for 2h at 900°C in

air, respectively. The cooling was performed at slow rate in furnace. As-calcined powders were soaked in water at 60°C for 16h and rinsed repeatedly to wash off residual NaCl and then dried at 95°C for 1h.

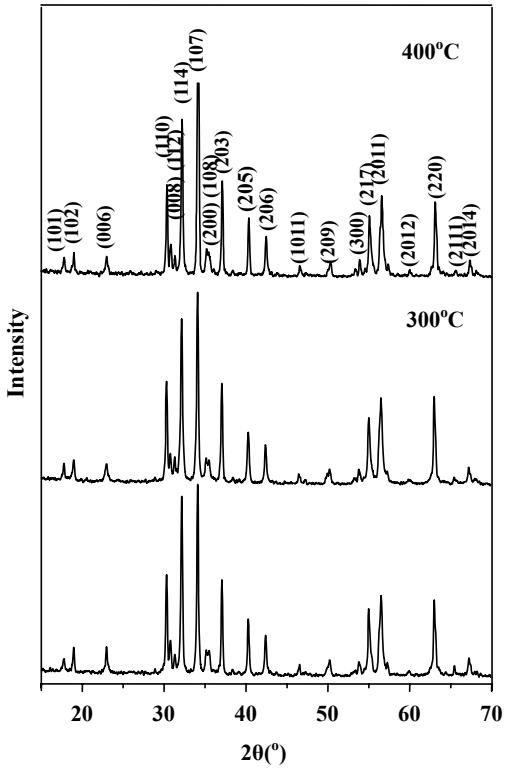

Fig.1. The XRD patterns of the $BaTiCoFe_{10}O_{19}$ powders preheated at different temperature.

The phase indentification of the calcined Ti-Co-substituted Ba-ferrite powders were conducted at room temperature using X-Ray diffractometer (XRD, CuK α_1, λ=0.15406nm, Model No. D/Max-2200PC, Rigaku, Japan). The phase and the particle sizes of powders were determined with the Jade5 analysis software carried with X-Ray diffractometer. Scanning electron microscopy (SEM, Model No: JXM-6700F, Japan) was used to analyses the particles morphology and the agglomeration of the powder.

3. Results and discussion

To investigate the effects of preheat treatment on formation and anisotropy of the M-type $BaTiCoFe_{10}O_{19}$ powders, dried hydroxide precursors were preheated for 1h at 300°C and 400°C respectively and then calcined for 2h at 900°C. As-calcined powders were characterized using X-Ray diffractometry. The XRD patterns of the powders were showed in figure1 and indicated that $BaTiCoFe_{10}O_{19}$ were only XRD detectable phase. The average particle sizes of the powders were determined with strong peak (114) at 2θ~34.1° in the XRD patterns and showed in Table 1. The average particle size of powder without preheat treatment was 38.7nm, the average particle sizes of powder preheated at 300°C and 400°C were 38.4nm and 40.8nm respectively. The preheat treatment at 300°C and 400°C resulted in a small decrease and increase in the average particle size of the powders respectively. Labarbe and co-workers[8] reported similarly that the saturation density of nuclei is higher and the size of crystalline is less for the lower nucleation temperature of glass-ceramics.

Table 1. The particle sizes(D) and lattice constant of the powders preheated at different temperature (T_p), determined with the data of the XRD analysis.

		lattice parameter			particle ize(nm)
ferrite	T_p(°C)	a(Å)	c(Å)	c/a	D
$BaTiCoFe_{10}O_{19}$		5.8905	23.2168	3.9415	38.7
	300	5.8925	23.2140	3.9396	38.4
	400	5.8891	23.2261	3.9440	40.8
$BaFe_{12}O_{19}$*		5.892	23.183	3.9347	

*The $BaFe_{12}O_{19}$ single crystal

The microwave property of M-type doped Ba-ferrites is dependent on their magnetocrystalline anisotropy energy, and the magnetocrystalline anisotropy energy is dependent on the atomic lattice anisotropy of these ferrites[5]. The lattice constant were calculated using the d, h, k and l value corresponding to (110), (008), (006), (107), (114), (203), (205), (217), (2011) strong peaks in the XRD patterns according to:

$$\frac{a^2}{d^2} = \frac{4}{3}\left(h^2 + hk + k^2\right) + l^2\frac{a^2}{c^2}$$

As calculated constant a and c value and c/a ratio of the $BaTiCoFe_{10}O_{19}$ powders with and without preheat treatment were showed in Table1. For comparison the lattice constant of $BaFe_{12}O_{19}$ powder was also showed in table1. Although the lattice constant a does not change significantly with the Co-Ti-substitution, the constant c

increases drastically with the substitution, as a result atomic lattice anisotropy of the powders were remarkably increased with the substitution. This may be attributed to the larger ionic radius of Ti^{4+} (0.68 Å), and Co^{2+} (0.72 Å) compared to Fe^{3+} (0.64 Å). This is in accordance with the fact that all hexagonal classes (M-, Y- and W-type) are characterized by constant lattice parameter a but varied parameter c[9]. The average c/a ratio decreased from 3.9415 to 3.9397 when preheating the sample at 300°C, but increased to 3.9440 at preheating temperature of 400°C. This may be attributed to a change of the formation process of the $BaTiCoFe_{10}O_{19}$ powders.

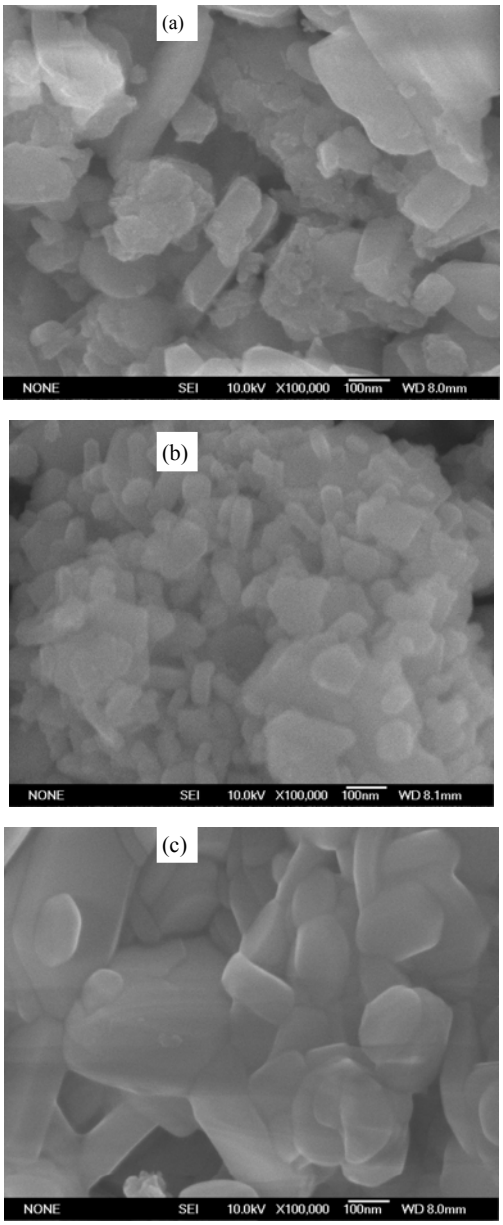

Fig. 2. SEM photographs of the $BaTiCoFe_{10}O_{19}$ powders (a) non – preheated and (b) preheated at 300 °C and (c) preheated at 400 °C (repeation 2).

Fig. 2 illustrate the SEM photographs of the $BaTiCoFe_{10}O_{19}$ powders. The degree of particles agglomeration of three powders was very weak. Three particles exhibited much small platelets with 20-40nm of thickness and 20-400nm of width and 20-150nm of average particle size. Among them the average particle size of powders preheated at 300°C was obviously less than the average sizes of two other powders. The dependence of the particle size on the preheat treat was accordant with result of the XRD analysis. The aspect ratio in morphology of the particles non-preheated, especially the partticles preheated at 400°C, were less than that of powders preheated at 300°C. The decrease in aspect ratio was accordant to the increase in the c/a ratio with change from preheating at 300°C to non-preheating and to preheating at 400°C. The platelike particles with smaller aspect ratio in morphology were most suitable for application of microwave absorption materials, as reported by Kreisel and co-workers[5].

4. Conclusion

The Ti-Co-substituted M-type Ba-hexaferrites powders were successfully prepared with sol-gel method. The anisotropy of the Ba-hexaferrites was drastically increased by Ti-Co-Substitution. The relations between the anisotropy and particle size of the $BaTiCoFe_{10}O_{19}$ powders and the preheat treatment were respectively showed.

The particle size $BaTiCoFe_{10}O_{19}$ powders were closed to theoretical single domain size about 40nm, which, together with higher atomic lattice anisotropy, smaller aspect ratio in morphology, larger crystallinity and less agglomeration, make the $BaTiCoFe_{10}O_{19}$ powders were very suitable for the microwave applications.

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