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ORIGINAL ARTICLE

Preheating Effects on the Particle Size and Anisotropy of M-type $BaAl_2Fe_{10}O_{19}$ Powders prepared via Sol-Gel Method

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ABSTRACT

Al-substituted M-type hexaferrite is a material with a high anisotropy. Use of this type of material in microwave absorber requests the powder possess high anisotropy field and platelike morphology with small aspect ratio. In this paper, we report the synthesis of $BaAl_2Fe_{10}O_{19}$ powder by a coprecipitation process and the effects of preheating temperature on the anisotropy of the powders. The powders were characterized using XRD and SEM. The XRD analysis indicated that the preheat treatment at 300ºC is favorable for the formation of single phase substituted M-type $BaAl_2Fe_{10}O_{19}$. The particle sizes of the powders were closed to 40nm and affected by preheat treatments. Calculation of c/a value with XRD data indicated that the Al-substitution and preheat treatment induced notable changes of the atomic lattice anisotropy.

Key word: $BaAl_2Fe_{10}O_{19}$; powder; sol-gel method; preheat treatment; c/a ratio; anisotropy

Introduction

M-typed hexaferrite exhibits a excellent magnetic property, a relatively high magnetocrystalline anisotropy field and platelike morphology. These make this type of ferrite very suitable for application in microwave materials and microwave absorber. The hexaferrites especially are best micro-wave absorber materials among various ferrites. Some cation substitutions can further change the anisotropy. Choi *et al* (2003) reported that the magnetocrystalline anisotropy field of the $BaAl_xFe_{12-x}O_{19}$ powder can be increased from $1.35*10^3$kA/m to $3.98*10^3$kA/m with increasing x=0 to x=4.

The properties of the substituted barium ferrites may be largely dependent on the characters of the powders except for substitution rate, increase as increase in magnetic anisotropy and shape anisotropy and crystallinity, and decrease in particle size. Many process routes have been devised for the preparation of a hexaferrite powder with refined particle size, narrow particle-size distribution, minimal particle agglomeration, and high crystallinity, including hydrothermal process (Komarneni, S., M.C. D'Arrigo, 1998), microemulsion technique (Pankov, V., 1997) et al. The characters of powders were affected by technological factors in processes of preparing the ferrite powders 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, Kreisel and co-workers (Kreisel, J., H. Vincent, 2001) present that the magnetic structure in doped Ba-hexaferrites changed drastically when the calcining temperature was altered. Preheat treatment also may affect the formation process of Al-substituted hexaferrites powders and further affect the anisotropy of the powders. However this effect has not been reported previously.

The Sol-gel method has advantages of low cost and simple technological process and is a useful method to prepare ultrafine Al-substituted hexaferrite 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 c/a value and particle size and formation of the Al-substituted M-type Ba-ferrite powders prepared by sol-gel method.

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2. Experimental Procedure
(1). Preparation of hydroxide Precursor

The ferric nitrate ninhydrate and barium chloride dihydrate and aluminium chlorite hexahydrate at a Ba^{2+}: Al^{3+}: Fe^{3+} ratio of 1: 2: 10 were dissolved in the solution containing ethanol and water at ratio of 1:1 and stabilized with little acetylaccetone to prevent titanium propoxide from hydrolyzing and stirred for 0.5h. In this solution, the molar concentrations were 0.0002M for Ba^{2+} cation, 0.0004M for Al^{3+} cation and 0.002M for Fe^{3+} cation, respectively. Then, sodium hydroxide aqueous solution was dropwisely slowly added into the solutions at room temperature with a constant stirring condition until pH=9-10. After the coprecipitation was completed, the precipitate slurry was filtrated and washed with anhydrous ethanol until pH~7 and dried for 10h at 100ºC.

(2). Heat Treatment and powder characterization

Two portions of as-dried precursor were preheated at 300ºC and 400ºC for 1h respectively. As-dried precursor and as-preheated precursors were heated at heating rate of 30ºC/min and calcined at 900ºC for 2.5h in air, respectively. The cooling was performed at a slow rate in furnace.

The phase indentification of the calcined $BaAl_2Fe_{10}O_{19}$ powders was conducted at room temperature using X-Ray diffractometer (XRD, $CuK_{\alpha 1}$, λ=0.15406nm, Model No: D/Max-2200PC, Rigaku, Japan). Scanning electron microscopy (SEM, Model No: JXM-6700F, Japan) was used to analysis the particles morphology and the agglomeration of the powder.

3. Results and Discussion

Figure 1 shows the XRD patterns of the powders. $BaAl_2Fe_{10}O_{19}$ is only XRD detectable phase for the sample preheated at 300ºC, however small amount of $BaFe_4O_7$ phase still present in other two samples. The $Fe(OH)_3$ in hydroxide precursor can be transfer to stable γ-Fe_2O_3 at 300ºC and to α-Fe_2O_3 at 400ºC. The γ-Fe_2O_3 with cubic spinel structure has similar structure with a $Fe(Fe_{5/3}\square_{1/3})O_4$ unit, in which $\square$ represents a cation vacancy, in the hexagonal $BaFe_{12}O_{19}$ structure, and so is easily transformed to the hexaferrite by reaction with $BaCO_3$ and BaO(Wei Zhong, 1997). However, once the α-Fe_2O_3 is formed, the complete conversion of the mixture to the single-phase hexaferrite requires a higher temperature because a need of a structure transformation(Wei Zhong, 1997). Without preheating, the $Fe(OH)_3$ in hydroxide precursor requires to firstly be transfer to γ-Fe_2O_3 and/or α-Fe_2O_3 in the process of the calcining. But many substituted M-ferrite powders can be perfectly synthesized with and without same preheating for calcining time of 2h, as reported in previous literatures[6-8]. By comparison, the synthesis of the pure $SrAl_4Fe_8O_{19}$ powder in condition of non-preheating and preheating at 400ºC may requests the longer calcining time. This may be due to the effect of suppressing crystallization of Al_2O_3 with very small melting entropy that results in weak crystallization property(He Haiyan, 1999). The average particle size of the powders was calculated with Scherrer's formula and showed in table 1. The particle size of the powders is changed from 34.3nm to 45.3nm, 43.4nm when preheating sample at 300ºC and 400ºC respectively. These sizes are close to the single-domain size (40nm) of M- type ferrite. The size of the powder without preheating is below the single-domain size of 40nm. The size of sample preheated at 400ºC also is less than that of the sample preheated at 300ºC. These may be duo to un-complete reaction to pure $BaAl_2Fe_{10}O_{19}$ powder. Figure 2 illustrate the SEM micrographs of the $BaAl_2Fe_{10}O_{19}$ powders. Three particles exhibited much small platelets with 20-80nm of thickness and 20-800nm of width and 20-240nm of average particle size. Scherrer's formula is only available in crystalline size range of 1-100 nm, the result calculated by Scherrer's formula is also affected by widening of diffraction peak resulted from micro-strain and dislocation in crystalline particle. The real particle sizes of the synthesized powders should be the results determined by SEM analysis.

The microwave property of M-type doped Ba-ferrites is dependent on their magnetocrystalline anisotropy energy, and that is dependent on the atomic lattice anisotropy of these ferrites. The lattice constant were calculated using the d, h, k and l value corresponding to (110), (008), (107), (114), (203), (205), (206), (209), (217), (2011) strong peaks in the XRD patterns according to:

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

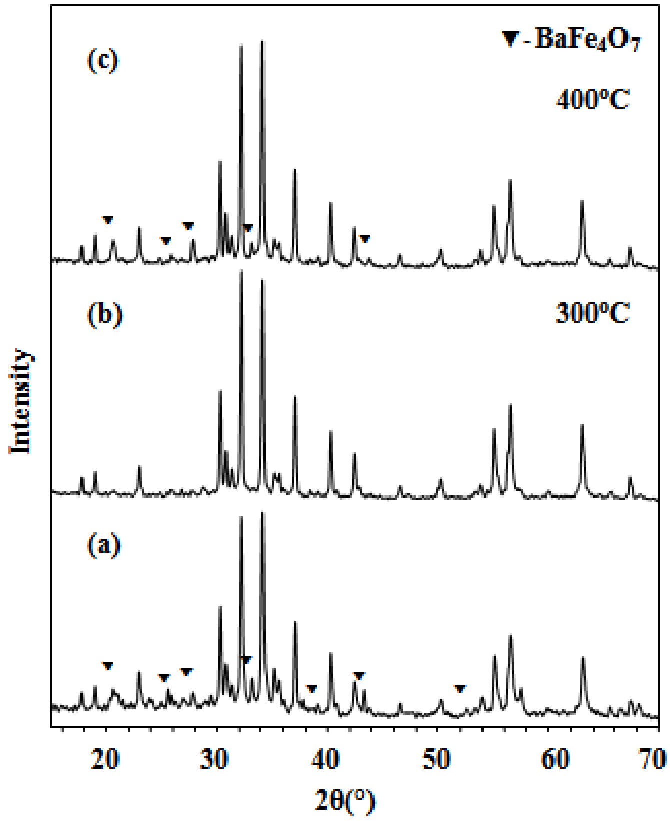

Fig. 1: XRD patterns of the $BaAl_2Fe_{10}O_{19}$ powders (a) non-preheated and (b) and (c) preheated at 300°C and 400°C

As calculated constant a and c value and c/a ratio of the $BaAl_2Fe_{10}O_{19}$ powders with and without preheat treatment were showed in table1. For comparison the lattice parameter of $BaFe_{12}O_{19}$ crystal was also showed in table1. The c/a ratio changed from 3.9425 to 3.9405 and 3.9382 at the preheating temperatures of 300°C and 400°C respectively. These ratios are all larger than that of the $BaFe_{12}O_{19}$ powders, indicating Al-substitution is greatly increased the atomic lattice anisotropy of the powder.

Figure2 illustrate the SEM photographs of the $BaAl_2Fe_{10}O_{19}$ powders. The degree of particles agglomeration of three powders was very weak. The powder preheated at 300°C was of larger average particle size than the two other powders. This may be due to completely reaction to the pure powder. The powder preheated at 300°C exhibited narrower particle-size distribution than the two other powders. The dependence of the particle size on the preheat treatment was accordant with result of the XRD analysis. The aspect ratio in morphology of preheated at 300°C, were less than that of particles non-preheated and particles preheated at 400°C. The platelike particle with smaller aspect ratio in morphology is most suitable for application in microwave absorption materials, as reported by Kreisel and co-workers (2001).

4. Conclusion

The M-type $BaAl_2Fe_{10}O_{19}$ ferrites powders were successfully prepared with sol-gel method. The anisotropy of the Ba-hexaferrite powders is greatly increased by Al-Substitution. The preheating of 300°C is available for the synthesis of pure $BaAl_2Fe_{10}O_{19}$ powder. The particle sizes of the powders were closed to a theoretical single domain size about 40nm, which, together with high atomic lattice anisotropy, can ensure a good microwave property and microwave absorbing property for the powders.

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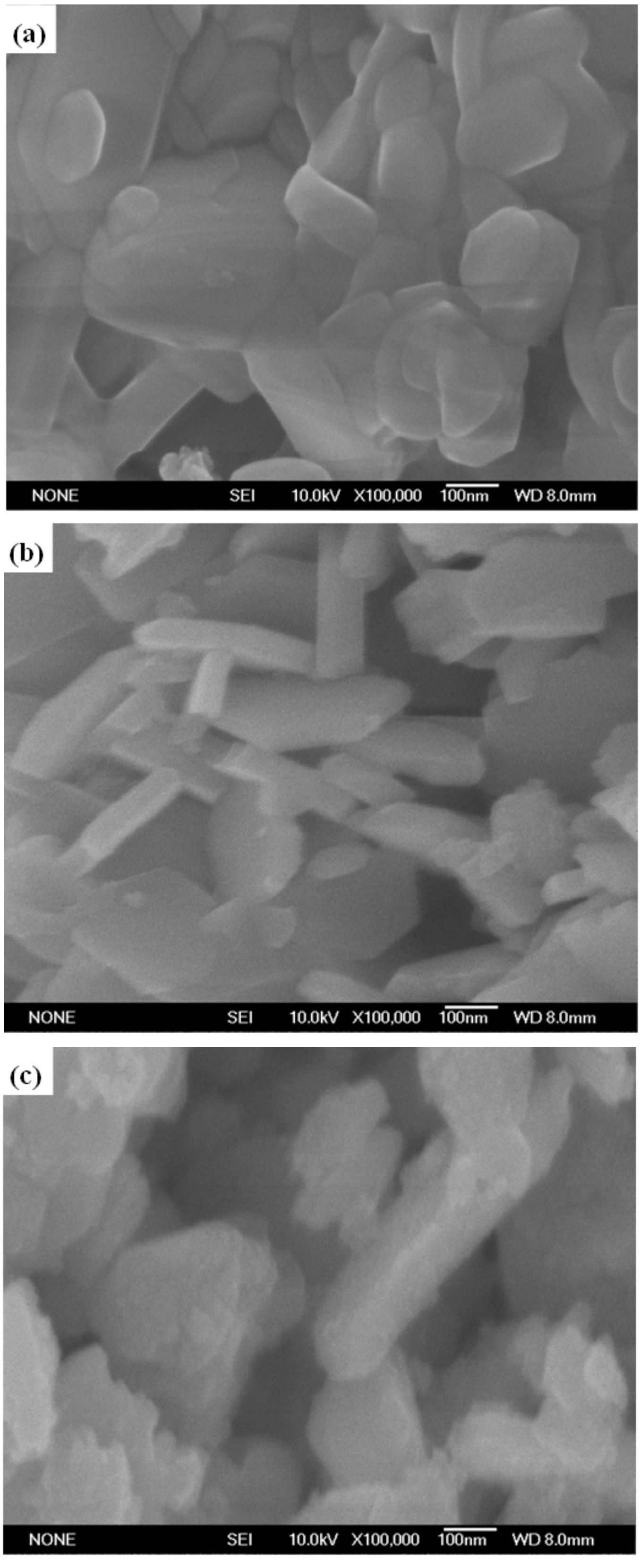

Fig. 2: SEM micrographs of the $BaAl_2Fe_{10}O_{19}$ powders (a) non-preheated and (b) and (c) preheated at 300ºC and 400ºC

Table 1: The c/a ratio and particle sizes of the $BaAl_2Fe_{10}O_{19}$ powders preheated at different preheating temperature (T_p), determined with XRD data analysis

Sample	T_p	a	c	c/a	particle size (nm)
$BaAl_2Fe_{10}O_{19}$		5.8865	23.2080	3.9425	34.3
	300ºC	5.8834	23.1836	3.9405	45.3
	400ºC	5.8882	23.1888	3.9382	43.4
$BaFe_{12}$O19		5.892	23.183	3.9347	

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