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Preheating effects on the particle size and anisotropy of M-type $Sr(TiMn)_2Fe_8O_{19}$ powders prepared by co-precipitation method

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Ultrafine substituted M-type Sr-ferrite $Sr(TiMn)_2Fe_8O_{19}$ powders were synthesized successfully by co-precipitation method. The hydroxide precursor particles were formed in gel solution containing ethanol and water at a ratio of 1:1 and NaOH as coprecipitation agent. The effects of preheat treatment on particle size and c/a value of $Sr(TiMn)_2Fe_8O_{19}$ nano powders were studied using XRD and SEM. XRD analysis indicated single phase substituted M-type Sr-ferrite $Sr(TiMn)_2Fe_8O_{19}$ were formed with and without preheat treatment. The particle sizes of the powders were very small with and without preheat treatments. Calculation of c/a value with XRD data indicated that the Ti-Mn substitution and preheat treatment induced notable change of the atomic lattice anisotropy.

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Keyword: $Sr(TiMn)_2Fe_8O_{19}$, powder, Sol-gel method, Preheat treatment, Anisotropy, Particle size

1. Introduction

M-typed 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 platelike morphology that can be used for many challenging applications, such as for a high-density type perpendicular recording media [1] and microwave materials and microwave absorber materials.. The hexaferrites are especially best micro-wave absorber materials among various ferrites. Some cation substitutions can further change the anisotropy. Sugimoto et al [2] reported that Ti-Mn-substituted Ba-ferrite $Ba(TiMn)_xFe_{12-2x}O_{19}$ (x=1.75-2) prepared via solid phase syntheses showed excellent absorbing property at X-band. Meng et al [3] reported that $Ba(TiMn)_2Fe_8O_{19}$ nano-particles with particle size below 100 nm were synthesed via coprecipitation-molten salt method and its absorbing property at 9.2-12.2GHz were larger than that of the micrometer particles. The M-type Sr-ferrite have a saturation magnetization of 74.3 emu/g and magnetocrystalline anisotropy field of 1.51×10^3 kA/m larger than 72.0 emu/g and 1.35×10^3 kA/m of M-type Ba-ferrite respectively and is also excellent microwave materials and microwave absorber.

The properties of the substituted strontium ferrites are largely dependent on the characters of the powders except for substitution rate, increase as increase in magnetic anisotropy and decrease in particle size and increase in crystallinity. 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 [4], microemulsion technique [5] et al. The characters of powders were influecnced 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 [6] present that the magnetic structure in doped Ba-hexaferrites changed drastically when the calcining temperature was altered. Preheat treatment also may influence the formation process of Ti-Mn substituted hexaferrites powders and further influence 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 usefull method to prepare ultrafine Ti-Mn-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 Ti-Mn-substituted M-type Sr-ferrite powders prepared by sol-gel method.

2. Experimental procedure

(1) Preparation of hydroxide Precursor

The ferric chloride hexahydrate and strontium carbonate and manganese chlorite tetrahydrate and titanium propoxide at a Sr^{2+}: Mn^{2+}: Ti^{4+}: Fe^{3+} ratio of 1: 2: 2: 8 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 0.5 h. In this solution, the molar concentration were 0.002M for Sr^{2+}cation, 0.004M for Mn^{2+}, and Ti^{2+} cation and was 0.016 M for Fe^{3+} cation, respectively. Then, sodium hydroxide aqueous solution was dropwisely slowly added into the 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 ^{o}C.

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(2) Heat treatment and powder characterization

Two partions of as-dried precursor were preheated at 300 ^{o}C and 400 ^{o}C for 1h respectively. As-dried precursor and as-preheated precursors were heated at heating rate of 25 ^{o}C/min and calcined for 2h at 900 ^{o}C in air, respectively. The cooling was performed at slow rate in furnace.

The phase indentification of the calcined Ti-Mn-substituted Sr-ferrite powders were conducted at room temperature using X-Ray diffractometer (XRD, $CuK_{\alpha 1}$, λ=0.15406 nm, Model No. D/Max-2200PC, Rigaku, Japan). Scanning electron microscopy (SEM, Model No: JXM-6700F, Japan) was used to analysie the particle 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 $Sr(TiMn)_2Fe_{10}O_{19}$ powders, dried hydroxide precursors were preheated for1h at 300 ^{o}C and 400 ^{o}C and then calcined for 2 h at 900 ^{o}C. As calcined powders were characterized using X-Ray diffractometry. The XRD patterns of the powders are shown in figure 1 which indicated that $Sr(TiMn)_2Fe_{10}O_{19}$ were only XRD detectable phase. The average particle sizes of the powders were determined with strong peak (114) at 2θ~34.1^{o} in the XRD patterns and showed in table 1. The particle size of powder were changed from 40.8nm to 39.8 nm and 41.1 nm when the samples were preheated at 300 ^{o}C and 400 ^{o}C respectively. The preheat treatment at 300 ^{o}C and 400 ^{o}C resulted in a small decrease and increase in the particle size of the powders respectively. Labarbe and co-workers [7] reported similarly that the saturation density of nuclei is higher and the size of crystallites is less for the lower nucleation temperature of glass-ceramics.

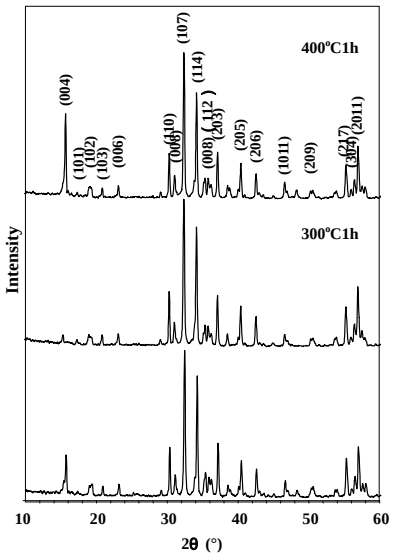

Fig. 1. The XRD patterns of $Sr(TiMn)_2Fe_8O_{19}$ nano-particles without preheat treat and with preheat treat at 300 ^{o}C and 400 ^{o}C, respectively.

Table 1. The particle sizes and c/a ratio of the ferrites powders preheated at different preheat treat temperature(T_p), determined with the data of XRD analysis.

			lattice parameter		
ferrite	T_p(^{o}C)	particle size(nm)	a(Å)	c(Å)	c/a
$Sr(TiMn)_2Fe_8O_{19}$		40.8	5.8906	23.0597	3.9145
	300	39.8	5.8922	23.0874	3.9183
	400	41.1	5.8914	23.0665	3.9153
$SrFe_{12}O_{19}$*			5.887	23.037	3.9132

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

The microwave property of M-type doped Sr-ferrites is dependent on their magnetocrystalline anisotropy energy, and the magnetocrystalline anisotropy energy 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), (1011), (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 $Ba(TiMn)_2Fe_{10}O_{19}$ powders with and without preheat treatment were showed in Table 1. For comparison the lattice parameter of $SrFe_{12}O_{19}$ single crystal was also showed in Table 1. The lattice constant a and c of the ferrite powders increased drastically with the Ti-Mn-substitution. This may be attributed to the larger ionic radius of Ti^{4+} (0.68 Å), and Mn^{2+} (0.80 Å) compared to Fe^{3+} (0.64 Å). The c/a ratio changed from 3.9145 to 3.9183 and 3.9153 at the preheating temperatures of 300 ^oC and 400 ^oC respectively. A largest value was achieved at preheating temperature of 300 ^oC.

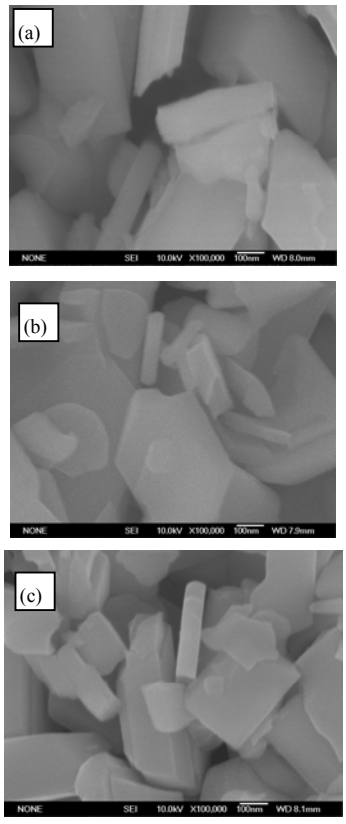

Fig. 2. SEM micrographs of the $Sr(TiMn)_2Fe_8O_{19}$ powders (a) non-preheated and (b) preheated at 300 ^oC and (c) preheated at 400 ^oC.

Fig. 2 illustrates the SEM photographs of the $Sr(TiMn)_2Fe_8O_{19}$ powder. The degree of particles agglomeration of three powders was very weak. Three particles exhibited much small platelets with 30-80 nm of thickness and 40-400 nm of width and 35-200 nm of average particle size. The aspect ratio in morphology of particles preheated at 300 ^oC was smaller than that of powders preheated at 300 ^oC which was smaller than powders non-preheated. The decrease in aspect ratio was accordant to the increase in the c/a ratio with change from non-preheating to preheating at 400 ^oC and to preheating at 300 ^oC. 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 [6].

4 Conclusions

The M-type Ti-Mn-substituted Sr-ferrites powders were successfully prepared with sol-gel method. The anisotropy of the Sr-hexaferrite powders was drastically changed by Ti-Mn-Substitution. The relations of the anisotropy and particle size of the Ti-Mn-substituted ferrites powders and the preheat treatments were showed.

The $Sr(TiMn)_2Fe_{10}O_{19}$ powders exhibit small particle size, which, together with high atomic lattice anisotropy, make the powders very suitable for various microwave applications.

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