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# Synthesis and magnetic properties of BaAl<sub>4</sub>Fe<sub>8</sub>O<sub>19</sub> powders fabricated by a microemulsion method

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Al-substituted M-type hexaferrite is a high anisotropy ferromagnetic material. In this paper, we report the synthesis and characterization of  $BaAl_4Fe_8O_{19}$  powders from two microemulsion systems of po1yoxyethylene octylphenol ether/1, 2-propylene glycol or ethanol/cyclohexane/water and cetrimonium bromide/1, 2-propylene glycol/cyclohexane/water. Two microemulsion systems were found to give wide stable regions. The synthesized powders were characterized with X-ray diffraction, scanning electron microscopy and a vibrating sample magnetometer. The experimental results indicated that the surfactant, co-surfactant, and oil/water ratio remarkably affected the particle size, size distribution, anisotropy and magnetic properties of the powders. The powder prepared with the microemulsion of po1yoxyethylene octylphenol ether/1, 2-propylene glycol/cyclohexane/water exhibited the best particle characters, that is, a uniform thin particle morphology, a large shape anisotropy, a small particle size, a large coercivity of 8734.16 Oe, and a saturation magnetization of 20.821 emu/g.

Key words: BaAl<sub>4</sub>Fe<sub>8</sub>O<sub>19</sub>, Microemulsion method, Anisotropy, Magnetic property.

### Introduction

M-typed hexaferrite possesses excellent magnetic properties, a relatively high magnetocrystalline anisotropy field and a plate-like morphology. This makes this type of ferrite very suitable for the applications as a microwave material and a microwave absorber. Some cation substitutions can further change the anisotropy. Aluminum substituted Bahexaferrite and Sr-hexaferrite powders all have an obvious enhancement in magnetiocrystlline anisotropy field, as reported by Choi *et al.* [1] and Heczko *et al.* [2].

The properties of the substituted hexaferrites are largely dependent on their characteristics, such as shape anisotropy, crystallinity, particle size and substitution rate [3]. Many process routes have been devised for the preparation of a hexaferrite powder with a refined particle size, narrow particle-size distribution, minimal particle agglomeration, and high crystallinity, including a coprecipitation method [3], a hydrothermal process [4], and an aerosol route [5] *et al.* 

The microemulsion method has an advantage of preparing ultrafine hexaferrite powders. In this paper, we present the formation, anisotropy, morphology and magnetic properties of the Al-substituted Ba-hexaferrite powders prepared with different microemulsion systems.

### **Experimental Procedure**

Starting materials used in this study were ferric nitrate

ninhydrate, barium chloride dihydrate, aluminium chlorite hexahydrate, po1yoxyethylene octylphenol ether (OP-10), cetrimonium bromide (CTAB), 1, 2-propylene glycol (PG), ethanol, NaOH and cyclohexane. All were analytical reagents.

### Fabrication of the ferrite powder

In this study, microemulsions consisted of either polyoxyethylene octylphenol ether (OP-10) or cetrimonium bromide (CTAB) as surfactants, 1, 2-propylene glycol (PG) and ethanol as cosurfactants, cyclohexane as the oil phase, and aqueous solutions of dissolved either metal ions or NaOH as water phases. The metal aqueous solution had a concentration of 0.0625 M for the  $Ba^{2+}$  cation, 0.25 M for the  $Al^{3+}$  cation and 0.5 M for the  $Fe^{3+}$  cation, respectively.

Phase diagrams of microemulsions for the two surfacants were determined at a constant surfactant molar ratio of OP-10: PG = 1:2, and CTAB: PG = 1:2, and are shown Fig. 1 and Fig. 2. It was found that the two systems gave wide stable regions. However, OP-10 system is only stable for a short time about 5 minutes in a usable region when PG was replaced by ethanol or isopropyl alcohol. On the phase diagrams, the weight ratio of oil : water : surfactants were selected as 7:3:4 and 7:3:3 respectively for the OP-10 system (Fig. 1) and the CTAB system (Fig. 2). In addition, a weight ratio of 5:5:4 was designed for a CTAB microemulsion as a low oil/water (O/W) ratio (Fig. 2). Because Al(OH)<sub>3</sub> is only stable at pH < 10, it is necessary to establish a largest NaOH concentration in the water phase. By repeat tests, a concentration of 2.6 M and 3.7 M of NaOH were determined as the largest NaOH concentrations respectively for the OP-10 and CTAB systems

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Fig. 1. Phase diagram of the OP-10 microemulsion system.



Fig. 2. Phase diagram of the CTAB microemulsion system.

After mixing the water phase solution and oil phase solution, the precipitate slurry was filtered and washed with anhydrous ethanol until pH $\sim$ 7 and dried at 100 °C for 10 h. The as-dried precursors were heated at a heating rate of 30 K·minute<sup>-1</sup>, and then calcined at 900 °C for 3 h in air. The cooling was performed naturally in a furnace.

## Characterization

The phase and structure of the calcined Al-substituted Sr-ferrite powders were identified at room temperature using an X-Ray diffractometer (XRD,  $CuK_{\alpha 1}$ ,  $\lambda = 0.15406$  nm, Model No : D/Max-2200PC, Rigaku, Japan). Scanning electron microscopy (SEM, Model No : JXM-6700F, Japan) was used to analyse the particles morphology of the powder. The magnetic properties were measured with a vibrating sample magnetometer (VSM, Model No : Versa Lab, Quantun Design, USA).

# **Results and Discussion**

Fig. 3 shows the XRD patterns of the synthesized powders. All samples were pure hexagonal M-type ferrite. The ferrite powders synthesized from the OP-10 microemulsion systems have (114) and (110) preferential orientations, while the powders synthesized from the CTAB microemulsion systems with high and low O/W ratio have a remarkable (107)-preferred orientation. This may be attributed to their special microstructure of the microemulsions.

The magnetic properties and microwave property of Al-substituted Sr-hexaferrites is theoretically dependent on their magnetocrystalline anisotropy energy, and that is dependent on the atomic lattice anisotropy of these ferrites. The lattice constants of the powders were calculated using the d, h, k and l value of strong peaks in the XRD patterns according to:

$$\frac{a^2}{d^2} = \frac{4}{3}(h^2 + hk + k^2) + l^2 \frac{a^2}{c^2}$$
(1)



**Fig. 3.** XRD patterns of  $BaAl_4Fe_8O_{19}$  powders synthesized with microemulsions of (a) OP-10/ethanol, (b) OP-10/ 2-propylene glycol, (c) CTAB (low O/W) and (d) CTAB (high O/W).

The as calculated lattice parameters *a* and *c* value and c/a ratio of the BaAl<sub>4</sub>Fe<sub>8</sub>O<sub>19</sub> powders are listed in Table 1. The microemulsion system obviously affected the c/a value. The c/a ratios of the samples synthesized with the OP-10 microemulsion were 3.9482 and 3.9394 respectively for co-surfactants of ethanol and PG. The c/a ratios of the samples synthesized with the CTAB microemulsion were 4.0588 and 3.9393 respectively for high and low O/W ratios

It can be observed from Fig. 4(a) and (b) that the precipitates prepared with OP-10/ ethanol and OP-10/PG microemulsions have respectively uniform and fluffy morphologies. The powders synthesized with the OP-10 microemulsion are very thin hexaplatelets (Fig. 4(c)). But the particles became nonuniform and larger when the cosurfactant PG was replaced by ethanol (Fig. 4(d)). The powders synthesized with the CTAB microemulsion with high and low O/W ratios have nanowire morphologies respectively with high and low aspect ratios (Fig. 5). The large difference in the particle morphology could come from the difference among the microstrucures of the microemulsions.

Fig. 6 shows the room temperature hysteresis loops of two samples prepared from the OP-10 microemulsion system. The saturation magnetizations of the BaAl<sub>4</sub>Fe<sub>8</sub>O<sub>19</sub> powders prepared with the co-surfactant ethanol and PG were 20.821 emu/g and 15.839 emu/g. The easy axis of



Fig. 4. SEM micrographs of the hydroxide precipitates prepared in (a) OP-10/ethanol and (b) OP-10/1, 2-propylene glycol microemulsions, and the  $BaAl_4Fe_8O_{19}$  powder prepared with (c) OP-10/ ethanol and (d) OP-10/PG microemulsions.



Fig. 5. SEM micrographs of the  $BaAl_4Fe_8O_{19}$  powder prepared with CTAB/PG microemulsions at O/W ratio of (a) 7 : 3 and (b) 5 : 5.



Fig. 6. Room temperature hysteresis loops of the powders prepared with OP-10 and different cosurfactants.

**Table 1.** Lattice parameters of  $SrAl_4Fe_8O_{19}$  powders determined from XRD data analysis

Sample -	lattice parameter			
	a(Å)	c (Å)	c/a	-
OP-10/ethanol	5.8660	23.1599	3.9482	
OP-10/PG	5.8770	23.1517	3.9394	
CTAB, High O/W	5.7834	23.4739	4.0588	
CTAB, Low O/W	5.8800	23.1631	3.9393	
				-

magnetization is parallel to the hexagonal *c*-axis. Thus, the mechanism for the variation in magnetization could be differences of the preferred crystal growth in the c-axis of easy magnetization and the particle size. The BaAl<sub>4</sub>Fe<sub>8</sub>O<sub>19</sub> powders prepared with the co-surfactant ethanol has a thicker particle morphology and a larger particle size (Fig. 4), and so has a larger saturation magnetization. The coercivity of the BaAl<sub>4</sub>Fe<sub>8</sub>O<sub>19</sub> powders prepared with the co-surfactants ethanol and PG were 3301.66 Oe and 8734.16 Oe. In general, magneto-crystalline anisotropy determines the achievable coercivity. The powder prepared with PG has a smaller atomic lattice anisotropy (Table 1), but a larger shape anisotropy and smaller particle size (Fig. 4). The variations in the coercivity with the shape anisotropy rather than the atomic lattice anisotropy of the ferrite particles are mainly because the shape anisotropy is the dominant form of the anisotropy when the particle size is smaller than 20 µm. The coercivity is a maximum at a single-domain size, beyond which there is a decrease in the coercivity. This may be another reason of the smaller coercivity of the powder prepared with the cosurfactant ethanol.

Fig. 7 shows the room temperature hysteresis loops of the powders prepared from the CTAB microemulsion system. The powders exhibited a weak ferromagnetic property with very a low permeability close to being linear. The coercivity of the BaAl<sub>4</sub>Fe<sub>8</sub>O<sub>19</sub> powders prepared at O/W = 7:3 and 5:5 were only 281.21 Oe and 277.45 Oe. This could be attributed to the strong (107)-oriented growth



**Fig. 7.** Room temperature hysteresis loops of the powders prepared with CTAB and different O/W ratios.

that did not produce enough orientational growth reaching single-domain size in each crystal axis.

## Conclusion

M-type  $BaAl_4Fe_8O_{19}$  powders were successfully prepared by a microemulsion method. The atomic lattice anisotropy, shape anisotropy, and magnetic properties of the powders varied remarkably with the surfactant, cosurfactant, and O/W ratio.

The powders prepared from the OP-10 system were of a uniform thin particle morphology, a higher shape anisotropy, a smaller particle size close to the theoretical single domain size. The cosurfactant PG is more effective than ethanol for a large shape anisotropy, a uniform thin particle morphology, a small particle size, and a large coercivity. The coercivity and magnetization of the powders varied with the shape anisotropy regardless of the atomic lattice anisotropy. The high coercivity implies a high anisotropic field, which in turn implies a high ferromagnetic resonance frequency. A small particle size might be effective to increase the reflection loss. Thus, the BaAl<sub>4</sub>Fe<sub>8</sub>O<sub>19</sub> powders prepared with the surfactant OP-10 and cosurfactant PG may be an excellent material for electromagnetic compatibility and other practical applications at high frequency. The powders prepared with CTAB were of nanowire morphology and exhibited a weak ferromagnetic property.

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