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Synthesis of Ba-ferrite microspheres doped with Sr for thermoseeds in hyperthermia

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M-type hexagonal ferrite, $MFe_{12}O_{19}$ (M = Ba, Sr, etc.) has been intensively investigated as a material for permanent magnets, high-density recording media, and microwave devices [1]. The sol-gel technique has emerged in recent years as a versatile method for synthesizing barium and strontium ferrite. The sol-gel technique offers the following advantages: the temperature needed for the crystallization process is lower, the particles produced are ultrafine, and they have a narrow size distribution [1]. Spray pyrolysis is a valuable technique for forming a non-agglomerated complex mixed-metal oxide powders with high purity, controlled stoichiometry and crystallinity, and a relatively narrow particle-size distribution [2]. Therefore, the sol-gel method prior to spray pyrolysis was used to prepare the samples for obtaining powders from a sol in much shorter periods compared to those needed using the traditional evaporation-drying procedure [3].

Appropriate portions of $Ba(NO_3)_2$, $(CH_3CO_2)_2Sr$, and $Fe(NO_3)_2 \cdot 9H_2O$ were dissolved in ethylene glycol, methyl alcohol and distilled water in the stoichiometric ratio, namely (Ba, Sr)/Fe = 1/10. The solution was refluxed at 80 °C for 12 hrs.

The spray pyrolysis equipment used in this study consisted mainly of an ultrasonic nebulizer (H556, LG Electronics, Korea), a furnace, a glass fiber filter (GF/F, Whatman, England) and a rotary pump [4]. The aerosol droplets were produced by ultrasonic frequency (1.67 MHz) and were nebulized at flow rates of 1–5 ℓ/min. The droplets were then passed through a low temperature first heating zone (300 °C) where the solvent was evaporated. The resulting dried particles were subsequently passed through a second heating zone (400–1000 °C) where the particles decomposed [5]. The powders were finally recovered by a glass fiber filter of 0.7 μm of pore size and were dried at 100 °C for 24 hrs. In order to study the changes in a crystalline phase, the sample was heat-treated at 300–1000 °C for 3–6 hrs.

The crystalline phases precipitated in the powder after spray pyrolysis and subsequent heat-treatment was determined by X-ray diffractometer (XRD; D/MAX Rint 2000, Rigaku, Japan) with Ni-filtered Cu-K_α rays and identified according to JCPDS. The morphology of the spray-pyrolyzed and heat-treated particles was examined using scanning electron microscopy (SEM; S2700, Hitachi, Japan). The saturation magnetization (Ms) and coercive force (Hc) of the heat-treated particles were determined under a magnetic field up to 1592 kA/m at room temperature using a

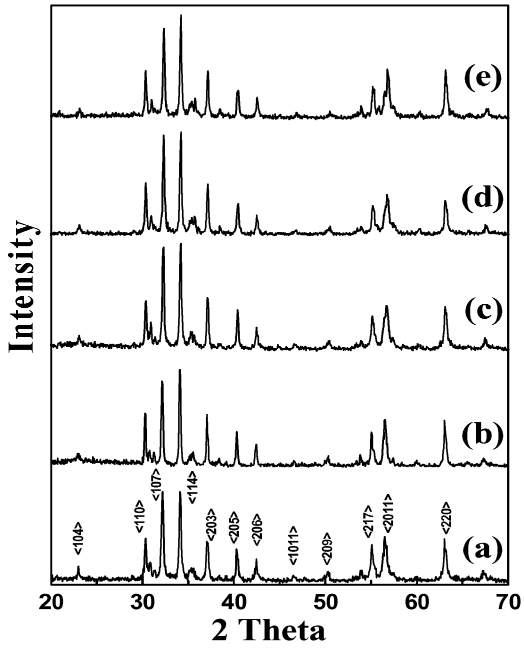

Figure 1 X-ray diffraction patterns of $Ba_{1-x}Sr_xFe_{12}O_{19}$ ferrites at various x of (a) 0, (b) 0.25, (c) 0.5, (d) 0.75, and (e) 1.0.

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TABLE I Crystalline phases of the spray-pyrolyzed and subsequent heat-treated microspheres

Spray pyrolysis (°C)	Subsequent heat-treatment	Crystalline phases
400		
1 ℓ/min	N/A	γ-Fe_2O_3
	300 °C, 3 hrs	Fe_3O_4
	700 °C, 6 hrs	α-Fe_2O_3, $SrFe_{12}O_{19}$
5 ℓ/min	N/A	FeO
	300 °C, 3 hrs	Fe_3O_4
	1000 °C, 6 hrs	$SrFe_{12}O_{19}$
1000		
1 ℓ/min	N/A	FeO, $SrFe_{12}O_{19}$
	300 °C, 3 hrs	γ-Fe_2O_3, $SrFe_{12}O_{19}$
	1000 °C, 6 hrs	$SrFe_{12}O_{19}$
5 ℓ/min	N/A	FeO, $SrFe_{12}O_{19}$
	300 °C, 3 hrs	γ-Fe_2O_3, $SrFe_{12}O_{19}$
	1150 °C, 6 hrs	$SrFe_{12}O_{19}$

vibrating sample magnetometer (VSM; 7300 Lakeshore, USA).

In the XRD diffraction patterns of the phase evolution of the powders according to the Sr^{2+}- substituted amount, increasing Sr^{2+}-substituted amount for Ba^{2+} decreased $BaFe_{12}O_{19}$ phase and increased $SrFe_{12}O_{19}$ phase (Fig. 1). Hysteretic loops for samples were measured. When Sr^{2+}-substituted completely for Ba^{2+}, coercive force was 565 kA/m and the saturation magnetization was 52 kA/m.

Table I shows the phase change of the samples at various spray pyrolysis and subsequent heat-treatment temperatures as well as flow rate of carrier gas. When flow rate of the carrier gas was 1 and 5 ℓ/min, γ-Fe_2O_3 and FeO phases were obtained by pyrolysis at 400 °C, respectively. However, pyrolysis at 1000 °C gave rise to a mixture of $SrFe_{12}O_{19}$, Fe_2O_3, and FeO. In this study, spray pyrolysis did not lead to a $SrFe_{12}O_{19}$ single phase. Therefore, in order to obtain the $SrFe_{12}O_{19}$ single phase, the spray-pyrolyzed particles were heat-treated subsequently at various temperatures. After spray pyrolysis at 400 °C, the Fe_3O_4 phase was obtained by subsequent heat-treatment at 300 °C for 3 hrs. The sample heat-treated at 300 °C for 3 hrs contained γ-Fe_2O_3 and $SrFe_{12}O_{19}$ phases after spray pyrolysis at 1000 °C. The $SrFe_{12}O_{19}$ single phase was obtained when the

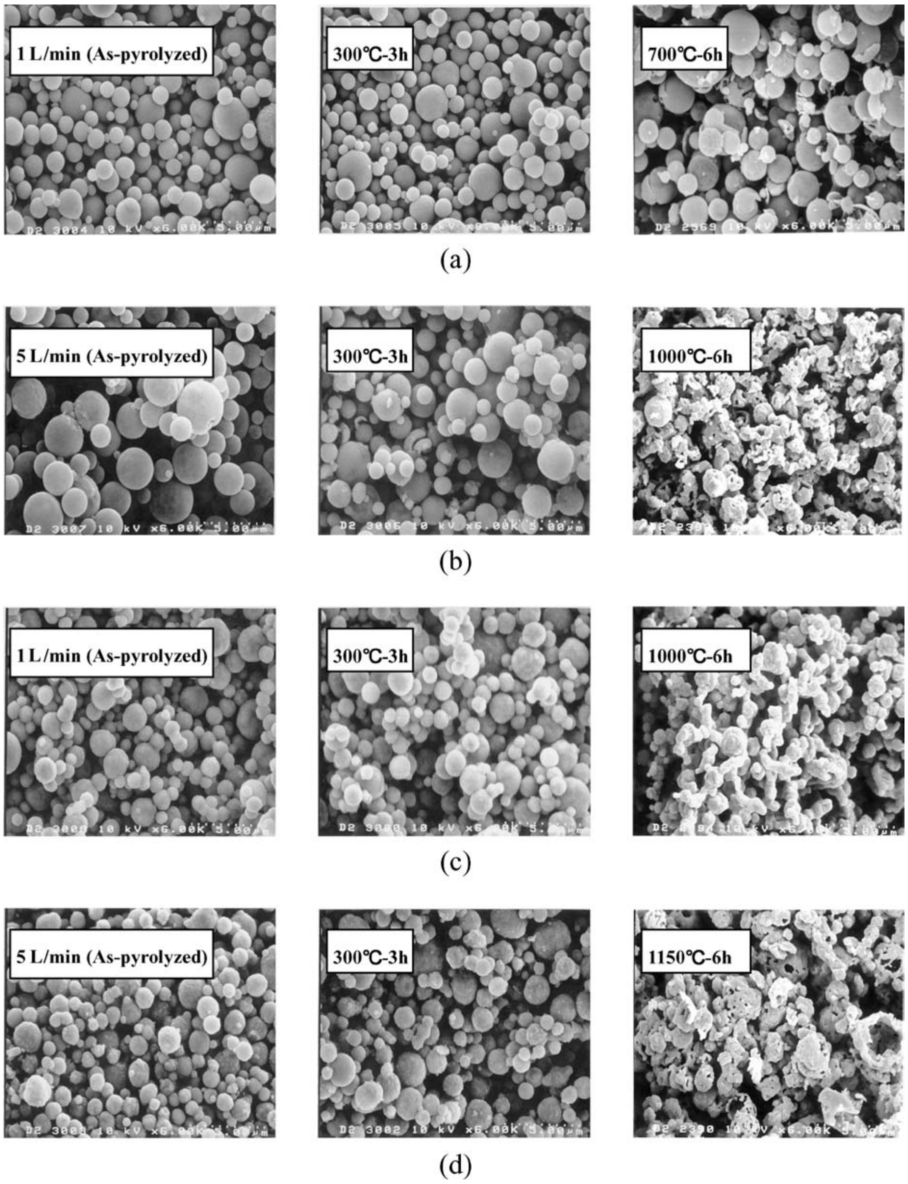

Figure 2 SEM micrographs of the spray-pyrolyzed powders at 400 and 1000 °C: (a) 400 °C, 1 ℓ/min, (b) 400 °C, 5 ℓ/min, (c) 1000 °C, 1 ℓ/min, and (d) 1000 °C, 5 ℓ/min.

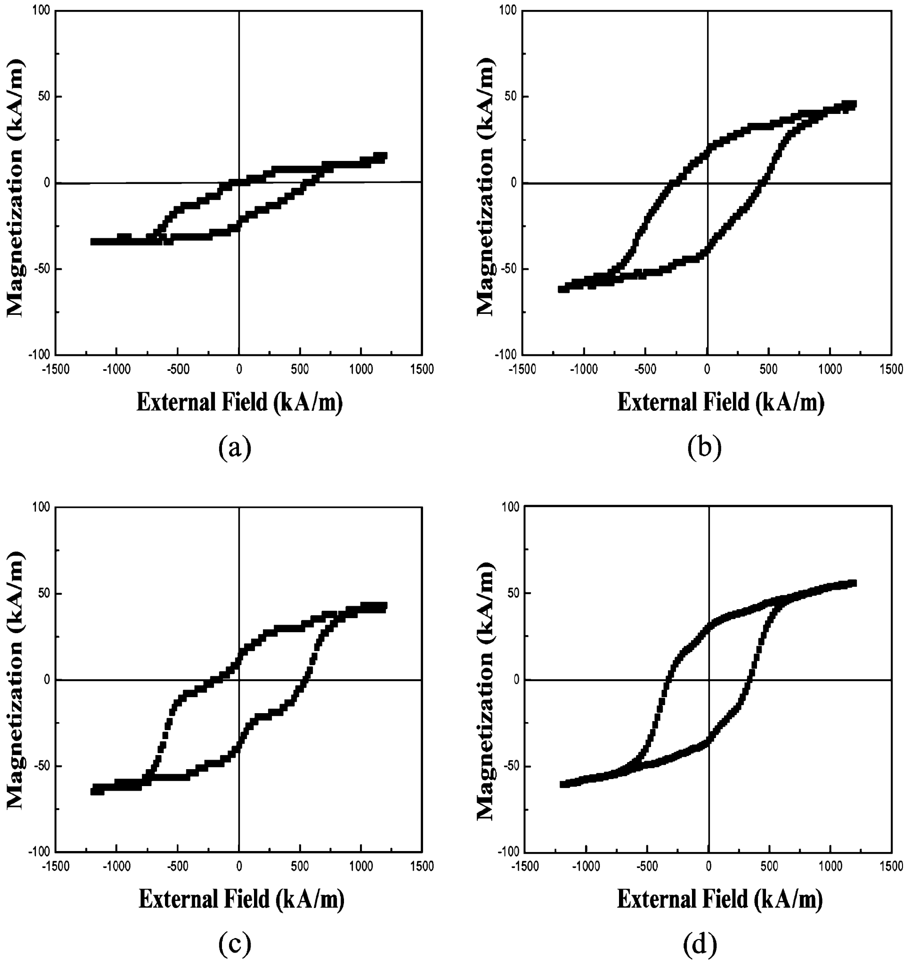

Figure 3 Hysteresis loops of the subsequent heat-treated for 6 hrs followed by spray pyrolysis: (a) 700 °C after 400 °C, 1 ℓ/min , (b) 1000 °C after 400 °C, 1 ℓ/min, (c) 1000 °C after 400 °C, 5 ℓ/min, and (d) 1150 °C after 1000 °C, 5 ℓ/min.

samples were heat-treated above 1000 °C after spray pyrolysis.

The particle size and morphology were examined using SEM for the spraypyrolyzed and heat-treated particles from 300 °C to 1150 °C (Fig. 2). The obtained particles were spherical after spray pyrolysis. Fig. 2a, b, c, and d show a mean particle size of 17.0, 13.9, 11.7, and 12.9 μm, respectively. However, particles were agglomerated after heat-treatment above 1000 °C. Fig. 3 shows particles heat-treated at 700 °C for 6 hrs after spray pyrolysis at 400 °C and 1 ℓ/min. The sample exhibited Ms = 52 kA/m and Hc = 39.79 kA/m. For the sample heat-treated at 1000 °C for 6 hrs after spray pyrolysis at 400 °C and 5 ℓ/min, Ms = 54.1 kA/m and Hc = 270.56 kA/m were observed. For the sample heat-treated at 1000 °C for 6 hrs after spray pyrolysis of 1 ℓ/min/1000 °C, Ms = 54.8 kA/m and Hc = 342.18 kA/m was observed. For the sample heat-treated at 1150 °C for 6 hrs after spray pyrolysis of 5 ℓ/min/1000 °C, Ms = 58 kA/m and Hc = 334.23 kA/m was observed. From the measured hysteretic loss one may easily estimate that the area of the hysteretic loops increases as the heat-treatment temperature increases by taking into account the relative crystallinity with increasing of $SrFe_{12}O_{19}$ content.

In order to verify the effects of Sr^{2+}-suubstitution to a Ba^{2+}-site, the synthesized $Ba_{1-x}Sr_xFe_{12}O_{19}$ microspheres with various compositions were examined. The synthetic process affects the material properties because the coercive force depends on the composition and the saturation magnetization depends on the anisotropy and stress [6]. Therefore, the highly pure sols were synthesized by the sol-gel methods. According to the atomic ratio Fe/Ba = 10, a suitable $Ba(NO_3)_2$ and $Fe(NO_2)_2{\cdot}9H_2O$ was added for transforming the $BaFe_{12}O_{19}$ particles. The hysteretic loops of the heat-treated particles were studied for the suitable amount of Sr^{2+}-substituted. The initial heat-treatment stage was 400 °C for 3 hrs, and the second heat treatment stage was 1000 °C for 6 hrs. γ-Fe_2O_3 phase appeared in the first heat-treatment stage, which is easy to transform to the $SrFe_{12}O_{19}$ phase [7, 8]. In spray pyrolysis, it is important to consider the melting points, solubility, volatilities, and reactivity of the precursors and all the possible intermediates as well as the relatively short time scale of the process to determine their effect on the phase evolution to the system [9]. However, the resident time in the furnace at 1000 °C of the aerosol droplets was too short to allow the total crystallization in this spray pyrolysis. Therefore, the spray pyrolysis temperature had to be higher, and the gas flow rate had to be longer (i.e., heating zone have a long distance or a vertical direction). Pyrolysis temperatures lower than 1000 °C gave rise to a phase mixture with γ-Fe_2O_3 and Fe_3O_4 being the most abundant. The value of specific magnetization was also greatest for single crystals of $SrFe_{12}O_{19}$ as obtained by spray pyrolysis followed heat-treatment at 1000 °C for 6 hrs.

When $x = 1$ in the $Ba_{1-x}Sr_xFe_{12}O_{19}$, Hc exhibited a maximum value of 565 kA/m, which is 79.58–119.37 kA/m higher than the previously reported values [10]. In this study, microspheres with mean size ranging from 11.7 to 17.0 μm could be synthesized by spray pyrolysis. The crystallinity showed that $SrFe_{12}O_{19}$ had a single phase according to the spray pyrolysis temperature and gas flow rate. In order to obtain the $SrFe_{12}O_{19}$ single phase, the samples needed to be heat-treated above 1000 °C. However, necking was observed in the gap of each microsphere. The spray-pyrolyzed microspheres calcined at 1000 °C for 6 hrs showing a single Sr-ferrite phase, the best magnetic properties of Ms = 54.8 kA/m, and Hc = 342.18 kA/m. Therefore, the prepared Sr-ferrite microspheres are expected to be useful thermoseeds in hyperthermic cancer-treatment because of their morphology and great hysteresis area.

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