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Composition and magnetic studies of ultrafine Al-substituted Sr hexaferrite particles prepared by citrate sol–gel method

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ABSTRACT

Ultrafine aluminum-substituted strontium hexaferrite particles have been prepared via citrate sol–gel route. Gels were synthesized with molar ratios $[Al^{3+}]:[Fe^{3+}]$ of 0.4:11.6, 1:11, 1.5:10.5 and 2:10 and the ferrite particles were obtained by annealing the gels at 950 °C for 2 and 24 h. Electron energy dispersive X-ray spectroscopy (EDX) verified the presence of Al in the substituted samples. X-ray diffraction (XRD) confirmed the formation of the M-type hexaferrite phase in the samples with some indication of α-Fe_2O_3. Scanning electron microscope showed that the hexaferrite powder consists hexagonal crystals with average diameter D_{av} (80–186 nm) that decreases with increasing Al content and increases with increasing annealing time. Magnetic properties were determined using a pulsed-field magnetometer and a vibrating sample magnetometer (VSM). The saturation magnetization at room temperature and the Curie temperature were found to decrease while the coercivity increases with increasing the Al content. The highest coercivity of 10.1 kOe was achieved for the sample with the molar ratio $[Al^{3+}]:[Fe^{3+}]=2:10$ annealed for 24 h. The influences of the particle size, composition and impurity on the magnetic properties were discussed.

1. Introduction

Barium and strontium M-type hexaferrites have been of considerable interest for many years due to their appropriate magnetic properties, chemically stability and low cost. The compounds are characterized by high magnetocrystalline anisotropy with single magnetization axis and used mostly for production of permanent magnets [1]. Research in this field recently focuses on those in the forms of thin films and ultrafine particles as they are promising candidates for high density magnetic data storage and micro devices [2–4]. For best performance, the particles should have a high magnetic coercivity, which depends on their chemical nature, shape and crystalline quality. High coercivity can be achieved in single domain particles with low defect concentration. On the other hand, it is known that partial substitution for Fe by Al in the strontium hexaferrite leads to a decrease of saturation magnetization M_s and also to an increase of magnetic anisotropy field H_a, hence higher coercivity in such materials can be obtained [5]. Previous works have reported the improvement of the magnetic characteristics of hexaferrite thin films and submicron particles via Al doping [6–8].

Ultrafine hexaferrite particles were prepared by mechanical alloying [8] and chemical methods such as sol–gel [9], coprecipitation [10], microemulsion [11] and oxide glass crystallization [7]. Submicron-sized barium hexaferrite exhibits coercivity of 5–6 kOe [8] and for those of strontium hexaferrite, coercivity is in the range of 6–7 kOe [9,12]. Recently reported values of the coercivity for the submicron particles with Al substitution are up to 9.3 kOe [8] and 10.18 kOe [7] for barium and strontium hexaferrites, respectively.

In our recent work [9], the formation of submicron La-substituted strontium hexaferrite particles via citrate sol–gel route was investigated with annealing temperatures between 650 °C and 1050 °C. The results showed that the single-phase samples can be obtained with annealing temperatures above 950 °C. The highest coercivities of 6.6 kOe and 7 kOe were achieved for the pure sample and for the substituted one, respectively. In the present paper, we report on the crystallization of ultrafine Al-substitute strontium ferrite particles using the same preparation method. Particle size and aluminum diffusion into the crystal lattice were examined by fixing the annealing temperature at 950 °C and varying the annealing time. The magnetic characters of the samples were investigated.

2. Experiments

Stoichoimetric amounts of $Fe(NO_3)_3$, $Sr(NO_3)_2$ and $Al(NO_3)_3$ were dissolved completely in deionized water. In these processes, $[Sr^{2+}]:[Fe^{3+}+Al^{3+}]$ was fixed at 1:12 and $[Al^{3+}]:[Fe^{3+}]$ was set to be 0.4:11.6, 1:11, 1.5:10.5 and 2:10. Each aqueous solution containing Sr^{2+}, Fe^{3+} and Al^{3+} was poured into citric acid with

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[citric acid]:[$Sr^{2+}+Fe^{3+}+Al^{3+}$]=3. Ammonium hydroxide in aqueous form was added to the mixed solutions and the pH of the solutions was adjusted to about 1. The mixtures were stirred at 1000 rpm and slowly evaporated at 80 °C to form gels. The gel products were heated in air at 450 °C for 2 h to form aerogels. Two batches of samples were obtained by annealing the aerogels in air at 950 °C for 2 h and 24 h.

X-ray diffraction (XRD) was employed to identify the crystal structure. Scanning Electron Microscopy (SEM) was used to examine the particle size and morphology. The elemental characterization was carried out using energy dispersive X-ray spectroscopy (EDX). Magnetic hysteresis loops of the samples at room temperature were measured by a pulsed-field magnetometer with maximum applied magnetic field up to ± 30 kOe. Temperature dependence of magnetization of the samples was measured using a Vibrating Sample Magnetometer (VSM) in temperature range 300–800 K and applied field up to 13 kOe. The powders were dispersed and fixed in epoxy for hysteresis loop measurements while for magnetization measurements at elevated temperatures the samples were pressed under the pressure of 4 t/cm^2 to form platelets.

3. Results and discussion

The XRD patterns of Al-substituted Sr hexaferrite samples in the form of $SrFe_{12-x}Al_xO_{19}$ after annealing at 950 °C for 2 and 24 h are shown in Fig. 1. For all the samples, the main phase has hexagonal structure with space group P6/3 mmc and matches well with the literature [13]. Small peaks at $2\theta=33.1°$ and 49.5° were observed in the samples $x=1$, 1.5 and 2 annealed for 2 h, which are typical of aniferromagnetic α-Fe_2O_3 and are characterized by Miller indices (104) and (024), respectively [14]. Such an observation was also reported by other authors [15] and may be attributed to the occurrence of local combustion during annealing. The intensity ratio between the most intense peak of the α-Fe_2O_3 phase at $2\theta=33.1°$ and that of the main hexaferrite phase at $2\theta=34.19°$ are in the range of 12–18%. From the XRD patterns of the samples, the lattice parameters a and c and unit cell volume V were calculated and shown Table 1. The lattice constants tend to decrease with increase in aluminum content, which is attributed to the smaller ionic radius of substituted Al^{3+} cation (0.535 Å) as compared to that of Fe^{3+} (0.64 Å).

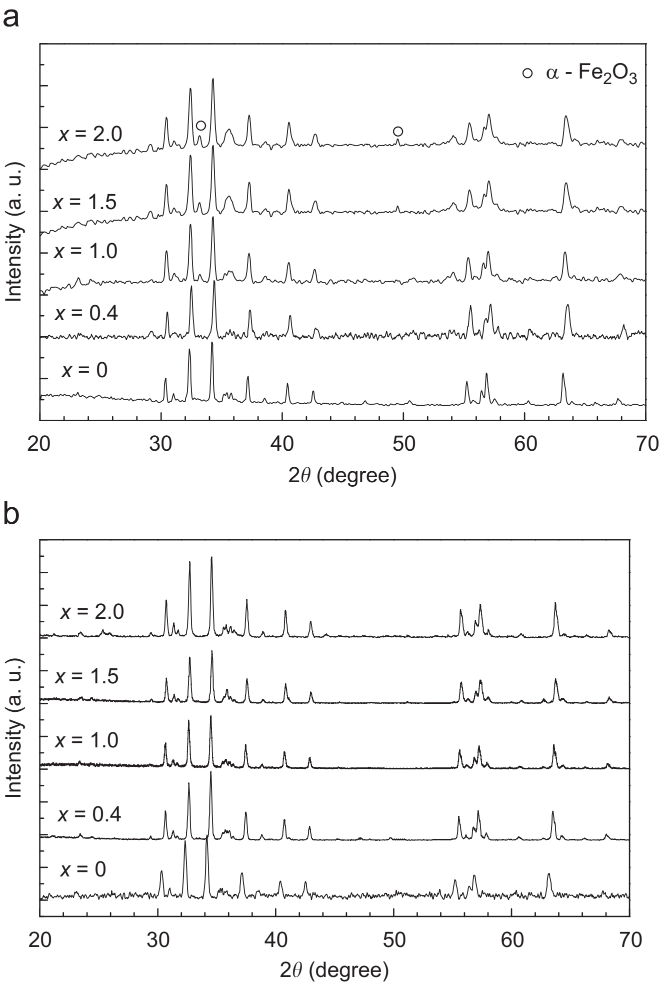

Fig. 1. XRD patterns for the $SrFe_{12-x}Al_xO_{19}$ samples (x=0, 0.4, 1, 1.5 and 2) annealed at 950 °C for (a) 2 h and (b) 24 h.

The SEM images of the samples are shown in Fig. 2. The results indicate that all the particles have a proper hexagonal platelet shape. From sampling of about 600 particles from different micrographs for each sample, the average diameters $\langle D \rangle$ of the samples were determined. As listed in Table 1, the average diameter decreases with increase of aluminum content and increase with increasing the annealing time. The decrease of grain size with increase of x was also observed for Al-substituted barium hexaferrite particles studied by Dhage et al. using a similar preparation method [16]. The results reveal that the Al^{3+} ions play a role in inhibiting the grain growth during heat treatment. The thickness and aspect ratio can be measured only for the particles, which were at the right angle to the micrograph plane. The average aspect ratio for these samples is found to be around 2.7.

Elemental analytical data for Sr, Fe and Al in the samples was obtained by EDX. Analysis was carried out at 6 different points of each sample. The compositions at different positions for all cases are close to one and another. Table 2 shows the average values of x, which match well with the formula ratio of the ferrites.

Density ρ_{XRD} of the samples were calculated based on the formula, $\rho_{XRD}=ZM/N_AV$, where Z is the number of chemical formula units in a unit cell (Z=2 for these samples), M the molar mass of the samples, V the unit cell volume and N_A Avogadro's number. The density value for each sample is listed in Table 1.

Hysteresis loops were measured at room temperature for all the samples from which the coercive field H_c, saturation magnetization M_s and remanent magnetization M_r values were obtained. The samples show high coercivity and a small susceptibility in high fields up to 30 kOe. Nonsaturation may be due to some fraction of superparamagnetic particles or contribution from the alignment of canted spin at the particle surfaces. For several substituted samples with short annealing time, this may also indicate the presence of α-Fe_2O_3 phase as observed via the XRD

Table 1
Lattice constants a and c, cell volume V, mean crystallite size $\langle D \rangle$ and X-ray density ρ_{XRD} of the $SrFe_{12-x}Al_xO_{19}$ samples annealed at 950 °C for 2 h and 24 h.

x	a (Å)	c (Å)	V (Å^3)	$\langle D \rangle$ (nm)	ρ_{XRD} (g/cm^3)
950 °C, 2 h					
0	5.880	23.202	694.721	140	5.07
0.4	5.873	23.078	689.505	125	5.06
1.0	5.863	23.03	685.543	110	4.99
1.5	5.851	23.007	682.151	100	4.95
2.0	5.848	22.951	679.746	80	4.92
950 °C, 24 h					
0	5.880	23.202	694.721	186	5.07
0.4	5.857	22.980	682.702	175	5.11
1.0	5.856	22.970	682.172	175	5.01
1.5	5.850	22.930	679.589	150	4.98
2.0	5.835	22.931	676.138	125	4.90