Sol–gel hydrothermal synthesis of strontium hexaferrite nanoparticles and the relation between their crystal structure and high coercivity properties

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Abstract

Hard magnetic strontium hexaferrite SrFe₁₂O₁₉ nanoparticles were synthesized by the sol–gel hydrothermal method. The factors affecting the synthesized process, such as the mole proportion of the reactants, pH, temperature, the hydrothermal conditions and the calcination process, have been investigated. The crystal structures of these materials were refined by Rietveld method. The obtained materials have single crystal phase, equal nano-size, plate shape and high anisotropy. The high magnetic coercivity of 6.3 kOe with the magnetization at 11.1 kOe of 66 emu g⁻¹ at room temperature was observed for the strontium hexaferrite nanoparticles. For other nanoparticles (SrLn₁₂₋₁O₁₉ and SrFe₁₂O₁₉/CoFe₂O₄) synthesized on the basis of SrFe₁₂O₁₉ the complex completion of the crystal structure distortion and the interaction between magnetic phases were observed.

Keywords: hexaferrite magnetic powder, sol–gel hydrothermal, magnetic nanomaterials, core–shell structure

Classification number: 5.02

1. Introduction

Hard magnetic hexagonal ferrite materials MFe₁₂O₁₉ (M = Ba, Sr) with magnetoplumbite structure have been widely applied in techniques to produce permanent magnets, loud speakers, microsized motors, actuators, micro wave devices, mini-pumps etc [1–3]. The advantages of these materials are the high coercivity, the moderate saturation magnetization and low price.

SrFe₁₂O₁₉ has crystal structure of hexagonal M-type ferrite. The M-type ferrite crystallizes in a hexagonal structure with 64 ions per unit cell on 11 different symmetry sites. Each unit cell contains 10 closely packed oxygen layers forming SRS * R* hexagonal blocks. The 24 Fe³⁺ atoms are distributed over five distinct sites: three octahedral sites (12k, 2a and 4f₂), one tetrahedral (4f₁) site and one bi-pyramidal site (2b). The Sr²⁺ ions are located in the R blocks. The magnetic structure given by the Gorter model is ferrimagnetic with five different sublattices, three parallel (12k, 2a and 2b) and two anti-parallel (4f₁ and 4f₂) which are coupled by super exchange interactions through the O²⁻ ions [4]. The replacement of the Sr²⁺ ions, which are non-magnetic and have large radius (1.18 Å) in crystal, by those with the same size and large charge such as La³⁺ (1.032 Å), or by a magnetic ion such as Sm³⁺ (0.958 Å), will induce deep changes of super exchange interactions between Fe³⁺ ions through the O²⁻ ion at 2b site because the substitution of Sr²⁺ by La³⁺ or Sm³⁺ reduces the oxidation number and distorts the bi-pyramidal sites containing Fe³⁺.

The magnetic properties of this material are related to the fabrication method, particles size and particle morphology. So in the research of nano-SrFe₁₂O₁₉ fabrication methods
Figure 1. XRD patterns of SrFe$_{12}$O$_{19}$ with different mole ratios of Fe$^{3+}$/Sr$^{2+}$. (a) SFO Fe$^{3+}$/Sr$^{2+}$ = 8; (b) SFO Fe$^{3+}$/Sr$^{2+}$ = 11 and (c) SFO Fe$^{3+}$/Sr$^{2+}$ = 12.

Figure 2. XRD patterns of SrFe$_{12}$O$_{19}$ samples with different mole ratios of AC/ΣMe. (a) SFO12, k = 1; (b) SFO12, k = 2; (c) SFO12, k = 3; (d) SFO11, k = 2; (e) SFO11, k = 3.

one should also care about high purity, ultrafine size, good dispersion and excellent magnetism [5–8]. The conventional method to create the SrFe$_{12}$O$_{19}$ particles is solid phase reaction at very high temperature. Besides the solid route, chemical wet methods such as co-precipitation, hydrothermal, sol–gel etc, have been developed [5, 7–10]. The substitution of Sr$^{2+}$ in SrFe$_{12}$O$_{19}$ crystal by rare earth ions (La$^{3+}$, Nd$^{3+}$, Sm$^{3+}$ . . .) or the reaction between hard magnetic phase (SrFe$_{12}$O$_{19}$) and a soft magnetic phase (CoFe$_2$O$_4$, NiFe$_2$O$_4$ . . .) induces changes of magnetic properties of SrFe$_{12}$O$_{19}$ [11–13].

In this paper, we present the sol–gel hydrothermal method for fabricating SrFe$_{12}$O$_{19}$ nanoparticles and the relation between crystal structure and hard magnetic properties of SrFe$_{12}$O$_{19}$ nanoparticles when the Sr$^{2+}$ ion was substituted by La$^{3+}$ and when the SrFe$_{12}$O$_{19}$ is the core of the core–shell structure material. The sol–gel hydrothermal method combines the advantages of the sol–gel method and the high pressure in the hydrothermal condition. In the hydrothermal process, the particle size and particle morphology can be controlled. SrFe$_{12}$O$_{19}$ nanoparticles have high purity, ultrafine size and high coercivity.

2. Experimental

2.1. Preparation of SrFe$_{12}$O$_{19}$ nanoparticles

The samples were prepared using the sol–gel hydrothermal method. Chemical-grade Fe(NO$_3$)$_3$·9H$_2$O, Sr(NO$_3$)$_2$ were used as pre-substances for preparing SrFe$_{12}$O$_{19}$ (SFO) nanoparticles. A suitable amount of Fe(NO$_3$)$_3$·9H$_2$O and Sr(NO$_3$)$_2$ was dissolved in distilled water to obtain Fe$^{3+}$ solution and Sr$^{2+}$ solution. These solutions were mixed in order to achieved the mole ratios of Fe$^{3+}$/Sr$^{2+}$ = 8, 11, 12. Then citric acid (AC) solution was added to the mixture in the mole ratios AC/ΣMe = k (k = 1, 2, 3; ΣMe is total mole of metal ions). The solution was stirred for about 1 h. The
2.2. Preparation of Sr

The calcination temperature varied the mole ratio Fe\(^{3+}\)/Sr\(^{2+}\) of SrFe\(^{2+}\) nanoparticles. To material’s magnetic properties, we prepared SrFe\(^{2+}\) nanoparticles. Lattice parameters and average crystallite size of SrFe\(^{2+}\) nanoparticles are shown in Table 1.

| Sample  | a (Å) | b (Å) | V (Å\(^3\)) | Rwp (%) | Rap (%) | Average crystallite size (nm) |
|---------|-------|-------|-------------|---------|---------|-----------------------------|
| SFO11,  | k = 2 | 5.87  | 5.87        | 23.00   | 686.88  | 7.13                        |
| k = 3   | 5.87  | 5.87  | 23.01       | 687.38  | 8.05    | 10.95                       |

In order to optimize the process of preparation of SrFe\(^{2+}\) nanoparticles and study the influences of preparation condition to material’s magnetic properties, we varied the mole ratio Fe\(^{3+}\)/Sr\(^{2+}\), the mole ratio AC/\(\Sigma\)Me and the calcination temperature.

2.3. Preparation of CoFe\(_2\)O\(_4\) nanoparticles

CoFe\(_2\)O\(_4\) nanoparticles were prepared by co-precipitation method. The mixed solution containing 50 ml of Fe\(^{3+}\) and Co\(^{2+}\) with the mole ratio Fe\(^{3+}\)/Co\(^{2+}\) = 2 was drop-by-drop added into the reaction vessel containing 100 ml of 1 M NaOH aqueous solution under vigorous stirring. The suspension was stirred for 2 h. The precipitate was then separated by a high-speed centrifuge at 6000 rpm, and then washed with Sr\(^{2+}\) solution. A suitable amount of La\(_2\)O\(_3\) was dissolved in to HNO\(_3\) solution to obtain La\(^{3+}\) solution. These solutions were mixed in order to achieved the mole ratio of Fe\(^{3+}\)/(La\(^{3+}\)+Sr\(^{2+}\)) = 12. The next steps of the preparation process were the same as for the preparation of SrFe\(^{2+}\) nanoparticles.

Table 1. Lattice parameters and average crystallite size of SrFe\(_{12}\)O\(_{19}\) samples.

Table 2. The atomic positions in the unit cell of SrFe\(_{12}\)O\(_{19}\).

![Figure 5. SEM micrograph of SrFe\(_{12}\)O\(_{19}\) phase (Fe\(^{3+}\)/Sr\(^{2+}\) = 11, k = 3, sintering at 1050 °C).](image1)

![Figure 6. Simulated XRD pattern by the Rietveld method of SrFe\(_{12}\)O\(_{19}\) nanoparticles (a) and Sr\(_{0.5}\)La\(_{0.5}\)Fe\(_{12}\)O\(_{19}\) nanoparticles (b).](image2)
distilled water. The washed sample was dried at 100 °C in air for 2 h and then was sintered at different temperatures.

2.4. Preparation of SrFe$_{12}$O$_{19}$/CoFe$_2$O$_4$ core/shell structure

The right amount of SrFe$_{12}$O$_{19}$ nanoparticles were dispersed in ethanol and sonicated for 10 min. Then NaOH solution of 1 M was used to activate the SrFe$_{12}$O$_{19}$ nanoparticles by ultrasonic irradiation. After pre-treatment the SrFe$_{12}$O$_{19}$ nanoparticles were separated by centrifugation. Then the SrFe$_{12}$O$_{19}$ nanoparticles were added into the boiling NaOH aqueous solution. The mixed solution containing Fe$^{3+}$ and Co$^{2+}$ with the mole ratio Fe$^{3+}$/Co$^{2+} = 2$ was drop-by-drop added into the reaction system and stirred for 2 h. The final product was separated by centrifugation, washed with distilled water, dried and sintered at different temperatures.

The magnetic properties of the products were observed using a vibrating sample magnetometer (VSM) at room temperature under a maximum field of 15 T. The reaction products were identified by x-ray diffraction (XRD) using Cu-Kα radiation and refined by Rietveld method using Rietan software. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to observe the grain size and morphology of the product.

3. Results and discussion

3.1. Characterization of SrFe$_{12}$O$_{19}$

3.1.1. Influence of the mole ratio Fe$^{3+}$/Sr$^{2+}$. SrFe$_{12}$O$_{19}$ nanoparticles were prepared with the mole ratio Fe$^{3+}$/Sr$^{2+} = 8, 11, 12$. The XRD results showed that the samples with Fe$^{3+}$/Sr$^{2+} = 11$ and 12 were single phase because we only observed the characteristic peaks of SrFe$_{12}$O$_{19}$. The diffraction peaks at 2θ values of 34.17°, 32.31°, 30.34°, 37.15°, 63.16° and 56.81° corresponded to the strongest diffraction planes (114), (107), (110), (203), (2200) and (2011). These patterns ascribed to hexagonal Sr–M hexaferrite SrFe$_{12}$O$_{19}$ phase. In the XRD patterns of sample with Fe$^{3+}$/Sr$^{2+} = 8$, besides the peaks of SrFe$_{12}$O$_{19}$, there were peaks of α-Fe$_2$O$_3$. The peaks at 2θ values of 33.17°, 35.66°, 54.06°, 49.46° and 24.14° reflected the presence of Fe$_2$O$_3$ phase. Figure 1 showed the XRD patterns of strontium M-ferrite powders with different Fe$^{3+}$/Sr$^{2+}$ mole ratio (8, 11 and 12) calcined at 1050 °C.

3.1.2. Influence of the mole ratio AC/ΣMe. SrFe$_{12}$O$_{19}$ samples (the ratio of Fe$^{3+}$/Sr$^{2+} = 11$ and 12) were prepared with different ratios of AC/ΣMe = k (k = 1, 2 and 3).

XRD patterns (figure 2) showed that all samples with AC/ΣMe = k = 1, 2, 3 had high purity, SrFe$_{12}$O$_{19}$ phase wasn’t mixed with any different phase. So, the mole ratio AC/ΣMe did not affect the singles phase of SrFe$_{12}$O$_{19}$ samples which were prepared by sol–gel hydrothermal method. However, the mole ratio AC/ΣMe affecting the magnetic properties of SrFe$_{12}$O$_{19}$ samples and will be presented in VSM measurement results.

3.1.3. Influence of the sintering temperature. The sintering temperature was determined by the thermal analysis. The thermal analysis result of SrFe$_{12}$O$_{19}$ (Fe$^{3+}$/Sr$^{2+} = 11$, k = 3) in the range 100–1200 °C is presented in figure 3.

The result shows that in the range of temperature of 200–500 °C the burning process of organic substances took place, at 500 °C, the burning process almost completed and total mass of sample reduced 72.45%. So the samples were preliminarily calcined at 500 °C. After the preliminary calcination, samples were sintered at temperatures of 550, 750 and 1050 °C. In the XRD patterns (figure 4) at 550 °C the only characteristic peak of α-Fe$_2$O$_3$ was observed. At the higher temperature, 750 °C, SrFe$_{12}$O$_{19}$ phase was formed, but a small amount of α-Fe$_2$O$_3$ was still observed. At the sintering temperature of 1050 °C, single phase of SrFe$_{12}$O$_{19}$ was formed. Figure 4 presents the XRD patterns of particle samples obtained after sintering at 550, 750 and 1050 °C.

Figure 5 is the SEM micrograph of SrFe$_{12}$O$_{19}$ phase (Fe$^{3+}$/Sr$^{2+} = 11$, k = 3, sintered at 1050 °C). One can observe that most of the particles are of hexagonal shape. The average crystallite size was calculated by the Scherrer equation

$$d = 0.9\lambda / \beta \cos \theta,$$

where d is average crystallite size; $\beta$—full width at half maximum (FWHM), $\lambda = 1.5406$ Å—wavelength of X radiation. The average crystallite size of SrFe$_{12}$O$_{19}$ is presented in table 1.

The Rietveld method of structure refinement with powder diffraction patterns using Rietan software is used to refine the SrFe$_{12}$O$_{19}$ structure. Calculated results showed that SrFe$_{12}$O$_{19}$ with structure belongs to the P$6_3$/mmc space group, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$ and lattice parameters a, b, c and V are reported in table 1. The $R_p$ and $R_{wp}$ values under 10% show that the product prepared by sol–gel hydrothermal method has single phase and no other phase can be observed.

Figure 6(a) is the XRD result which was refined by Rietveld method and the simulated structure of SrFe$_{12}$O$_{19}$.
nanoparticles sintered at 1050 °C and kept for 2 h. The positions of atoms in the unit cell were calculated and are reported in table 2. The result of particles sample is close to the calculated result for bulk sample [14].

3.2. Characterization of SrFe₁₂O₁₉/La₀.₃Fe₁₂O₁₉

Because of the same ion radius between Sr²⁺ and La³⁺, when La³⁺ is introduced into SrFe₁₂O₁₉ system it tends to substitute the Sr²⁺ position. Figure 6(b) is the XRD result which was refined by Rietveld method of the Sr₀.₈La₀.₂Fe₁₂O₁₉ nanoparticles sintered at 1050 °C and kept for 2 h. No peak of any phases was observed except the characteristic peak of hexagonal structure of P6₃/mmc space group. The bond length of Fe³⁺ ion and O²⁻ in the crystal does not change equally, but may increase or decrease depending on whether the tetrahedron or octahedron contains Fe³⁺ ions distortion. However, the decrease of bond length of Fe³⁺(2b)–O²⁻(2b) position is located in the same plane with M²⁺ in crystal) can be observed when La³⁺, whose ion radius is smaller than that of Sr²⁺, substitutes the Sr²⁺ position (table 3).

3.3. Characterization of SrFe₁₂O₁₉/CoFe₂O₄

Figure 7 is the XRD results of the shell sample (CoFe₂O₄), core sample (SrFe₁₂O₁₉) and core/shell sample (SrFe₁₂O₁₉/CoFe₂O₄). On the XRD pattern of core/shell sample (SrFe₁₂O₁₉/CoFe₂O₄) the existence of two phase SrFe₁₂O₁₀ and CoFe₂O₄ was observed.

The core/shell structure of SrFe₁₂O₁₀/CoFe₂O₄ and the morphologies of hexaferrite phase and spinel ferrite phase can be observed in the TEM and SEM photographs in figure 8. On the TEM of SrFe₁₂O₁₀/CoFe₂O₄ samples, one can observe the core–shell structure. The TEM results also show the dimension of the core–shell particles of SrFe₁₂O₁₀/CoFe₂O₄. The diameters of the core–shell particles are in the range of 265.86–354.22 nm, the diameters of the cores are in the range of 140.20–195.53 nm.

Table 3. The bond lengths between the atoms in the unit cell of Sr₀.₈La₀.₂Fe₁₂O₁₉.

| Chemical bonding          | SrFe₁₂O₁₀ | Sr₀.₈La₀.₂Fe₁₂O₁₀ |
|---------------------------|-----------|------------------|
| Fe(1)–O(4)                | 2.018     | 2.029            |
| Fe(2)–O(1)                | 2.057     | 2.035            |
| Fe(3)–O(2)                | 1.978     | 1.922            |
| Fe(3)–O(4)                | 1.894     | 1.895            |
| Fe(4)–O(3)                | 2.111     | 2.140            |
| Fe(4)–O(5)                | 1.971     | 1.859            |
| Fe(5)–O(1)                | 1.984     | 1.945            |
| Fe(5)–O(2)                | 2.049     | 2.080            |
| Fe(5)–O(4)                | 2.095     | 2.053            |
| Fe(5)–O(5)                | 1.796     | 1.952            |
3.4. Magnetic properties

Figure 9 shows the VSM results at room temperature of SrFe$_{12}$O$_{19}$ samples with Fe$^{3+}$/Sr$^{2+}$ being 11 (a) and 12 (b); k = 1, 2, 3 and sintered at 1050 °C. The magnetic properties of SrFe$_{12}$O$_{19}$ samples are reported in table 4.

Saturation magnetization of SFO samples with different mole ratios Fe$^{3+}$/Sr$^{2+}$ and Ac/ΣMe are not very different, but the SFO sample with the mole ratio Fe$^{3+}$/Sr$^{2+}$ = 11 and k = 3 has the highest saturation magnetization (Ms = 66 emu g$^{-1}$). This sample also has the highest coercivity ($H_C = 6315$ Oe). Other samples have high coercivity in the range of 4911–5665 Oe. The coercivity of SrFe$_{12}$O$_{19}$ depends on the anisotropy of the grain, and coercivity increases with the increase of anisotropy. It can be observed that the higher the mole ratio AC/ΣMe = k, the higher are the coercivity values.

Figure 10(a) is the hysteresis loops of SrFe$_{12}$O$_{19}$ and Sr$_{0.8}$La$_{0.2}$Fe$_{12}$O$_{19}$ nanoparticles prepared by hydrothermal method in the same conditions. The substitution of Sr$^{2+}$ by La$^{3+}$ created the change of coercivity. $H_C$ value of Sr$_{0.8}$La$_{0.2}$Fe$_{12}$O$_{19}$ is higher than that of SrFe$_{12}$O$_{19}$. Figures 10(b) and (c) are the hysteresis loops of the SrFe$_{12}$O$_{19}$/CoFe$_2$O$_4$ nanoparticles after calcination at 950 °C (figure 10(b)) and 1050 °C (figure 10(c)) for 2 h.

4. Conclusion

The SrFe$_{12}$O$_{19}$ and Sr$_{1-x}$La$_{x}$Fe$_{12}$O$_{19}$ nanoparticles were synthesized successfully by sol–gel hydrothermal method. The obtained products have single phase, particles have hexagonal shape, the right proportion and high coercivity. The Rietveld method of structure refinement with powder
diffraction patterns using Rietan software is used to determine the SrFe_{12}O_{19} and Sr_{1-x}La_{x}Fe_{12}O_{19} structure. The calculated results agree with experiment.

The SrFe_{12}O_{19} synthesis process by sol–gel hydrothermal method was optimized. SrFe_{12}O_{19} nanoparticles have high purity, ultrafine size and high coercivity ($H_c = 4911–6315$ Oe). Coercivity values depend on the mole ratios Fe^{3+}/Sr^{2+} and AC/ΣMe, samples with Fe^{3+}/Sr^{2+} = 11 and $k = 3$ has the highest coercivity ($H_c = 6315$ Oe). In the same synthesis conditions of mole ratio AC/ΣMe, pH, the sintering temperature, the coercivity of SrFe_{12}O_{19} is higher than that of Sr_{1-x}La_{x}Fe_{12}O_{19}.

The physical parameters of nanoparticles with core-shell structure SrFe_{12}O_{19}/CoFe_{2}O_{4} were calculated. The diameters of the core-shell particles are in the range of 265.86 nm–354.22 nm, the diameters of the cores are in the range of 140.20–195.53 nm. The core-shell structure was observed by TEM photographs.

The substitution of Sr^{2+} position by La^{3+}, the interaction between hard and soft magnetic phases and the synthesis method strongly affected the structure and magnetic properties of SrFe_{12}O_{19} nanoparticles.

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