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Article

Controlling the Composition and Magnetic Properties of Nano-SrFe₁₂O₁₉ Powder Synthesized from Oily Cold Mill Sludge by the Citrate Precursor Method

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Abstract: This paper proposes a new method for producing nano-SrFe₁₂O₁₉ powder by the citrate precursor route using solid waste as a source of iron. This solid iron-containing waste, which exists in the form of an oily sludge, is produced by a cold rolling mill. This sludge was first subjected to a process, including sulfuric acid leaching, oxidation, precipitation, and nitric acid leaching, to obtain an iron nitrate (Fe(NO₃)₃) solution. Next, the Fe(NO₃)₃ solution was mixed with a strontium nitrate (Sr(NO₃)₂) solution obtained by subjecting strontium carbonate to nitric acid leaching. Subsequently, citric acid, as chelating agent, and ammonia water, as precipitating agent, were added to the mixed solution to form a gel. The gel was dried and spontaneously combusted, then annealed at different temperatures for 2 h in flowing air. The effects of the Fe³⁺/Sr²⁺ molar ratio and annealing temperature on the formation, morphology, and magnetic properties of SrFe₁₂O₁₉ were investigated. The results showed that single-phase SrFe₁₂O₁₉ powder was obtained by decreasing the Fe³⁺/Sr²⁺ molar ratio from the stoichiometric value of 12 to 11.6 and increasing the annealing temperature to 1000 °C for 2 h. Adjustment of the Fe/Sr molar ratio to 12 and the annealing temperature to 900 °C enabled the magnetic properties to be optimized, including saturation magnetization (M_s) 80.2 emu/g, remanence magnetization (M_r) 39.8 emu/g, and coercive force (H_c) 6318 Oe.

Keywords: SrFe₁₂O₁₉; nanoparticles; citrate precursor method; industrial waste; magnetic properties

1. Introduction

The most important ferrite materials with permanent magnetic properties, M-type ferrites are widely used as magnetic recording media, microwave absorbers, magneto-optics, and other functional materials in practical applications, and they also hold promise for future use in catalysis, biology, and other fields [1–4]. Among the M-type ferrite materials, SrFe₁₂O₁₉ does not contain the toxic heavy metal Pb, which contributes considerably to the content of PbFe₁₂O₁₉. Moreover, the magnetic properties of SrFe₁₂O₁₉ are slightly superior to those of BaFe₁₂O₁₉ [5]. Therefore, SrFe₁₂O₁₉ has received sustained and extensive attention [6–8]. Traditionally, SrFe₁₂O₁₉ is prepared via a solid-state reaction process [9], which mainly involves ball milling of iron and strontium oxides, and subsequent roasting at high temperature (~1200 °C). Although this process is inexpensive and convenient, it is difficult to accurately control the chemical homogeneity, particle size distribution, and crystal defects, thereby resulting in unsatisfactory magnetic properties [10].

Attempts to overcome these problems have led to the development of non-traditional methods, such as co-precipitation [11], sol-gel [12], hydrothermal [13], molten salt-assisted [14,15], and citrate

precursor [16–18]. Among these methods, the sol–gel and citrate precursor methods enable raw materials to be mixed on the ionic level and subsequent crystallization at low temperature, resulting in the production of uniform nano-SrFe₁₂O₁₉ [12,19]. Compared with the sol–gel method using metal alkoxide as raw material, the citrate precursor method has a relatively low production cost and simple process. Therefore, the citrate precursor method is considered to be promising for large-scale production of high-performance nano-SrFe₁₂O₁₉. In recent years, the preparation of nano-SrFe₁₂O₁₉ by the citrate precursor method has become a popular research topic. Although these studies focused on different aspects, such as process improvement [20–23] and doping modification [16,18,24], almost all of these studies utilized chemically pure nitrates as starting materials.

The rapid development of modern industry has caused the disposal of industrial solid waste to become a matter of serious global concern. In view of the wide application range and huge annual demand for SrFe₁₂O₁₉, the production of SrFe₁₂O₁₉ from industrial solid waste is not only able to realize the large-scale utilization of solid waste, but also to significantly reduce the production cost of SrFe₁₂O₁₉. Therefore, related studies have aroused widespread interest. Hessien et al. [25] synthesized SrFe₁₂O₁₉ powder with maximum saturation magnetization (Ms) 74.15 emu/g, remanence magnetization (Mr) 38.95 emu/g, and coercive force (Hc) 3455 Oe, using Egyptian celestine ore as a source of strontium, via a co-precipitation method. Xie et al. [26] reported a method for preparing SrFe₁₂O₁₉ powder with Ms 52.7 emu/g, Mr 29.6 emu/g, and Hc 3346 Oe from industrial strontium slag by chemical co-precipitation. Oily cold rolling mill (CRM) sludge is a metallurgical by-product produced during the process of cold rolling strip steel. In our previous research [27], SrFe₁₂O₁₉ powder with Ms 62.6 emu/g, Mr 32.6 emu/g, and Hc 3199 Oe was prepared by a solid phase reaction using oily CRM sludge as the source of iron. To our knowledge, preparation of nano-SrFe₁₂O₁₉ powder from waste by the citrate precursor method has not yet been reported.

Thus, the aim of the present paper is to report the preparation of nano-SrFe₁₂O₁₉ powder using oily CRM sludge as a source of iron via citrate precursor method. In addition, we also investigated the effect of annealing temperature and Fe³⁺/Sr²⁺ molar ratio in the gel on the crystal structure, morphologies, and magnetic properties of nano-SrFe₁₂O₁₉ powder. The results of our study show that the proposed method presents a viable alternative for recycling industrial solid waste, and the results are helpful to understand how to control the composition and magnetic properties of nano-SrFe₁₂O₁₉.

2. Materials and Methods

2.1. Materials

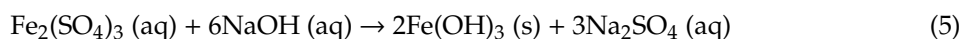
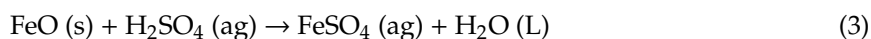
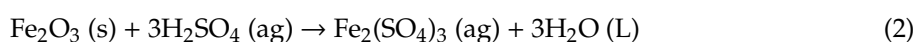
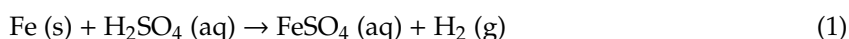
Chemically grade sulfuric acid (H₂SO₄, 95–98%), nitric acid (HNO₃, 65–68%), strontium carbonate (SrCO₃, ≥97%), sodium hydroxide (NaOH, ≥96%), hydrogen peroxide solution (H₂O₂, ≥97%), citric acid (C₆H₈O₇·H₂O, ≥99%), and ammonia water (NH₄OH, 25–28%), were used in this study. The oily CRM sludge used in this study was obtained from a plant that manufactures cold rolled strip in China. The main components of oily CRM sludge are provided in Table 1 together with their content.

Table 1. Main composition of oily cold rolling mill (CRM) sludge.

Component	Content (wt %)
Fe	70.6
Ni	0.049
Mn	0.18
Cr	0.065
Si	0.058
V	0.024
Oil and moisture	18.2
Other	10.82

2.2. Treatment of Oily CRM Sludge

To avoid the production of toxic nitrogen oxides by direct HNO_3 leaching, the oily CRM sludge was first leached by using 6 mol/L H_2SO_4 at 85 °C for 4 h under continuous agitation. The ratio of oily CRM sludge to acid was 1:5. After leaching, filtration and centrifugation were employed to separate the acid-insoluble matter and organic compounds from the leaching solution. Then, 30 wt % H_2O_2 was added drop wise to the leaching solution until Fe^{2+} was completely oxidized to Fe^{3+} . While stirring, 5 mol/L NaOH solution, which was used as precipitant, was added to the oxidized solution until the pH reached approximately 5. As a result, ferric hydroxide ($\text{Fe}(\text{OH})_3$) precipitated. The precipitate was removed by filtration and washed several times. Finally, solutions of ferric nitrate ($\text{Fe}(\text{NO}_3)_3$) and strontium nitrate were obtained after leaching the obtained $\text{Fe}(\text{OH})_3$ precipitates and SrCO_3 by using 8 mol/L HNO_3 , respectively. The above processes can be expressed as follows:



2.3. Preparation of Strontium Ferrites

Mixed solutions were prepared by varying the molar ratio of $\text{Fe}^{3+}/\text{Sr}^{2+}$ from 11.6 to 12 by proportionally mixing solutions of $\text{Fe}(\text{NO}_3)_3$ and $\text{Sr}(\text{NO}_3)_2$. Then, citric acid was added to the mixed solution until the molar ratio of citric acid to the sum of Fe^{3+} and Sr^{2+} reached 1.5. Subsequently, ammonia solution (25%) was added to the mixed solution to form a solution of pH 7. A viscous gel was obtained after magnetically stirring the solution for 4 h at 60 °C. The gel was dried at 100 °C overnight, and then burned spontaneously in air. Finally, $\text{SrFe}_{12}\text{O}_{19}$ powder was obtained after the combustion product was annealed at 400–1100 °C for 2 h in flowing air. The process flow chart of $\text{SrFe}_{12}\text{O}_{19}$ powder from oily CRM sludge is shown in Figure 1.

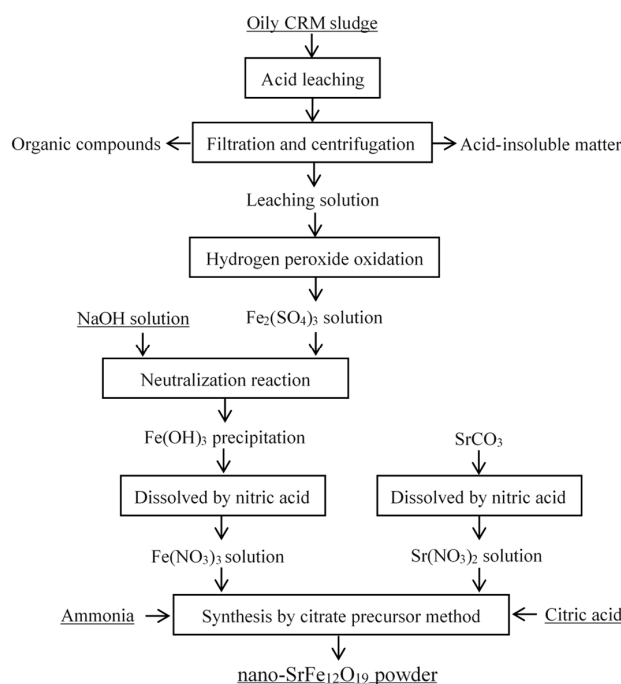


Figure 1. The process flow chart of $\text{SrFe}_{12}\text{O}_{19}$ powder obtained from oily CRM sludge.

2.4. Characterization

Inductively coupled plasma (ICP, OPTIMA 7000DV, PerkinElmer) was used to analyze the chemical composition of samples. The pH values of solutions were measured by a pH/mV meter (pHS-25, Huguang, China). The morphology of the products was observed by field-emission scanning electron microscopy (FE-SEM, Zeiss Ultra 55). Fourier transform infrared (FTIR) spectroscopy (Nicolet Nexus-470, Perkin-Elmer) was used to detect the types of functional groups present in the products. Thermogravimetric and differential scanning calorimetry (TG-DSC, STA409C, Netzsch) measurements of the samples were recorded at a heating rate of 10 °C/min in air. The magnetic properties of the obtained SrFe₁₂O₁₉ powder were assessed using a vibrating sample magnetometer (VSM, LDJ 9600) at room temperature. The hysteresis loops were used to determine the values of Ms, Mr, and Hc. The crystalline phases present in samples were identified by X-ray diffraction (XRD, APD-10, Philips). The mean crystallite size was determined using the Scherrer formula [28]:

$$d = K\lambda/\beta \cdot \cos\theta \quad (6)$$

where d is the mean crystallite size, K is a constant, β is the half width of the relevant diffraction reflection, λ is the X-ray wavelength, and θ is the diffraction angle. Moreover, the relative content of phases were calculated by the reference intensity ratio (RIR) method [29].

3. Results and Discussion

3.1. Effect of Annealing Temperature

The effect of the annealing temperature on the formation of SrFe₁₂O₁₉ was investigated by fixing the Fe³⁺/Sr²⁺ molar ratio of the gel at the stoichiometric ratio of 12. After combustion of the dried gel, the resulting material was first analyzed by FTIR and TG-DSC, respectively. The FTIR peak (Figure 2a) at 3300 cm⁻¹ is assigned to the vibration absorption of the O–H bond in citrate, which indicates the presence of citrate in the combustion products. The peaks at 1358 cm⁻¹ and 1416 cm⁻¹ are associated with the characteristic vibrational absorption band of NO₃⁻. The broadened absorption peak near 667 cm⁻¹ is the characteristic peak of γ -Fe₂O₃, which is associated with the Fe–O vibration. According to the TG-DSC analysis (Figure 2b), three distinct changes occur in the sample weight, that is, a small decrease below 280 °C, a significant decrease in the range of 280–470 °C, and stabilization above 470 °C.

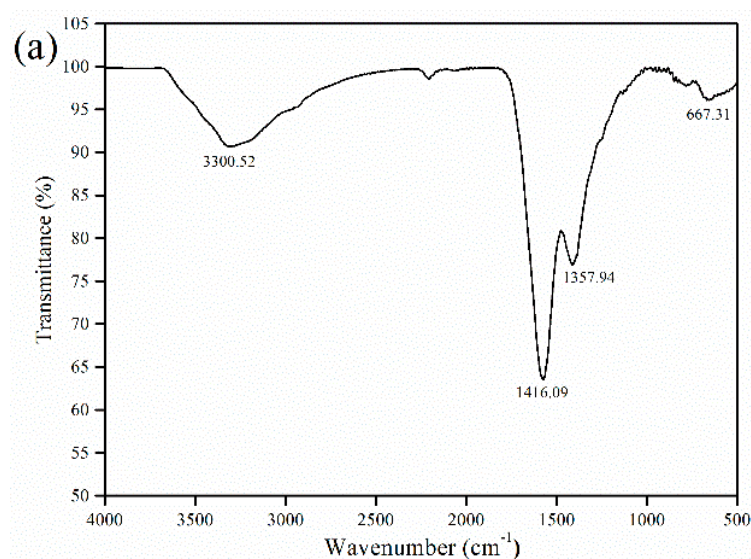


Figure 2. Cont.

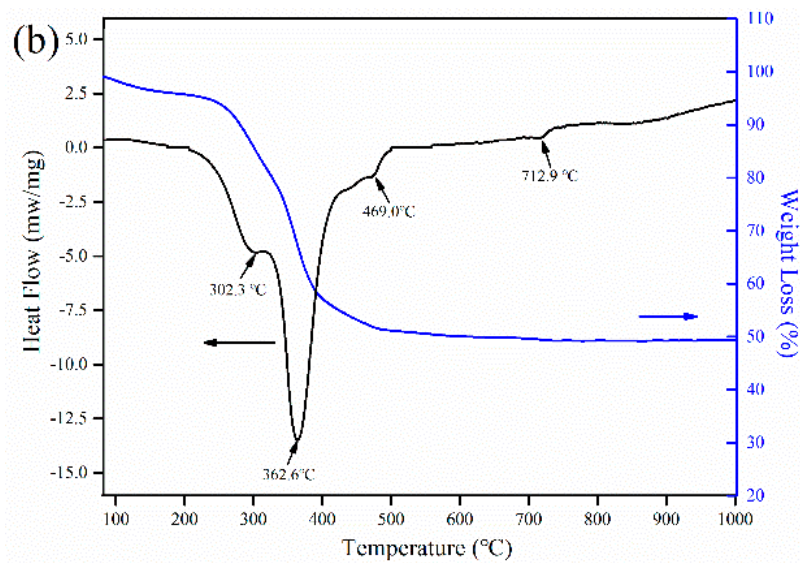
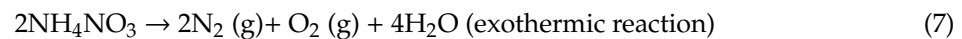


Figure 2. Analyses of the combustion products: (a) FTIR spectrum and (b) thermogravimetric and differential scanning calorimetry (TG-DSC) thermogram.

In view of the loose and porous structure of combustion products, the weight loss of the sample below 280 °C was mainly attributed to the evaporation of adsorbed moisture. Combined with the results of FTIR analysis, the significant weight loss at 280–470 °C was mainly caused by the decomposition of residual citrate, nitrate, etc. As the temperature rose above 362.6 °C, the thermal behavior of the sample changed from endothermic to exothermic. This indicates that the exothermic effect resulting from the decomposition of NH_4NO_3 (shown as equation (7)) begins to play a dominant role.



To further investigate the phase changes the samples undergo during heat treatment, a series of experiments was performed by varying annealing temperature from 400 to 1100 °C. XRD patterns of untreated and heat-treated samples are shown in Figure 3a.

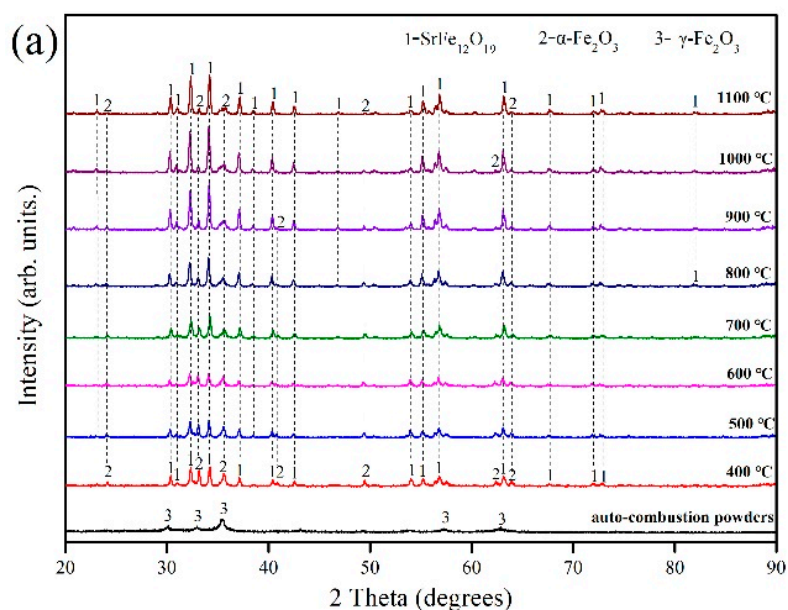


Figure 3. Cont.

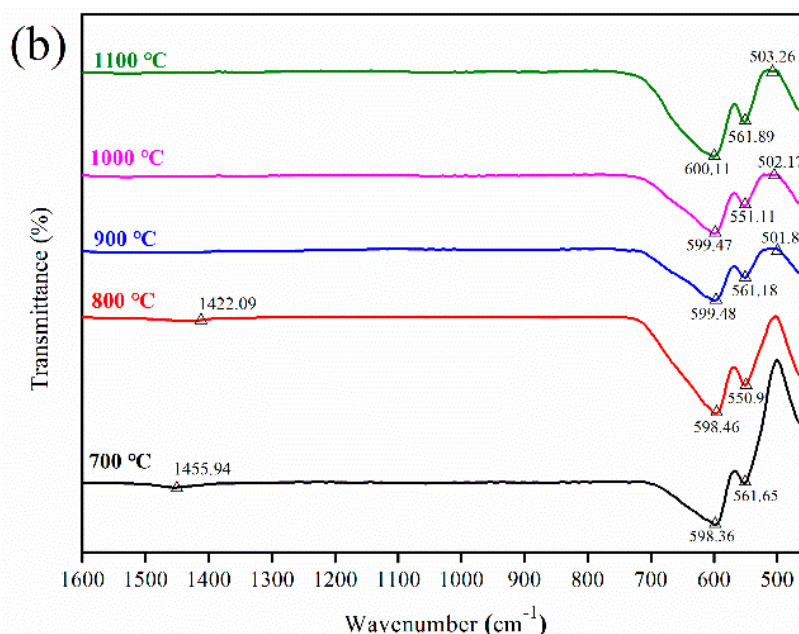


Figure 3. Analyses of untreated and heat-treated samples: (a) XRD patterns and (b) FTIR spectra.

The main crystal phase of the untreated sample was observed to be $\gamma\text{-Fe}_2\text{O}_3$, whereas the main crystalline phases of the sample annealed at $400\text{ }^\circ\text{C}$ are $\text{SrFe}_{12}\text{O}_{19}$ and $\alpha\text{-Fe}_2\text{O}_3$. This indicates that the following reaction occurs during the annealing process.



The intensity and resolution of the diffraction peaks of the $\text{SrFe}_{12}\text{O}_{19}$ phase in the samples increased as the calcination temperature increased, especially above $700\text{ }^\circ\text{C}$. The increased annealing temperature significantly reduced the number and intensity of the $\alpha\text{-Fe}_2\text{O}_3$ diffraction peaks in the sample. However, even at $1100\text{ }^\circ\text{C}$, a small amount of the $\alpha\text{-Fe}_2\text{O}_3$ phase still existed in the sample. The samples that were obtained at various temperatures from $700\text{ }^\circ\text{C}$ upward were further studied by recording their FTIR spectra (Figure 3b). The bands at 598.36 cm^{-1} , 598.46 cm^{-1} , 599.48 cm^{-1} , 599.47 cm^{-1} and 600.11 cm^{-1} correspond to the Sr–O stretching vibration band [30]. The bands at 561.65 cm^{-1} , 550.90 cm^{-1} , 561.18 cm^{-1} , 551.11 cm^{-1} and 561.89 cm^{-1} were attributed to the Fe–O stretching vibration by Fe–O₄ [31]. The bands at 501.83 cm^{-1} , 502.17 cm^{-1} and 503.26 cm^{-1} can be assigned to the Fe–O stretching vibrations of $\alpha\text{-Fe}_2\text{O}_3$ [32]. This indicates the existence of $\text{SrFe}_{12}\text{O}_{19}$ and $\alpha\text{-Fe}_2\text{O}_3$ in the samples, and is consistent with the results of the XRD analysis. Moreover, the samples obtained at $700\text{ }^\circ\text{C}$ and $800\text{ }^\circ\text{C}$ exhibited absorption peaks in the range $1400\text{--}1459\text{ cm}^{-1}$, and these peaks are associated with the characteristic vibrational absorption band of NO_3^- . This indicates that a certain amount of nitrate still existed in the samples below $900\text{ }^\circ\text{C}$, and that higher temperatures were helpful to remove them. Accordingly, this explains the 0.68% weight loss detected in the TG-DSC experiment.

The SEM images of the samples obtained at different annealing temperatures (Figure 4) show that the samples obtained at $700\text{ }^\circ\text{C}$ and $800\text{ }^\circ\text{C}$ had poor homogeneity with extensive agglomeration, indicating that the formation of $\text{SrFe}_{12}\text{O}_{19}$ was incomplete. These results are in good agreement with those of the XRD and FTIR analyses. Above $900\text{ }^\circ\text{C}$, samples were uniform with no obvious aggregation. The particle size of the sample annealed at $900\text{ }^\circ\text{C}$ were approximately 200 nm . With the increase of annealing temperature from 900 to $1000\text{ }^\circ\text{C}$, the particle size of the sample increased slightly. However, at $1100\text{ }^\circ\text{C}$, the powder particles clearly experienced abnormal growth. This may be due to the growth of particle size.

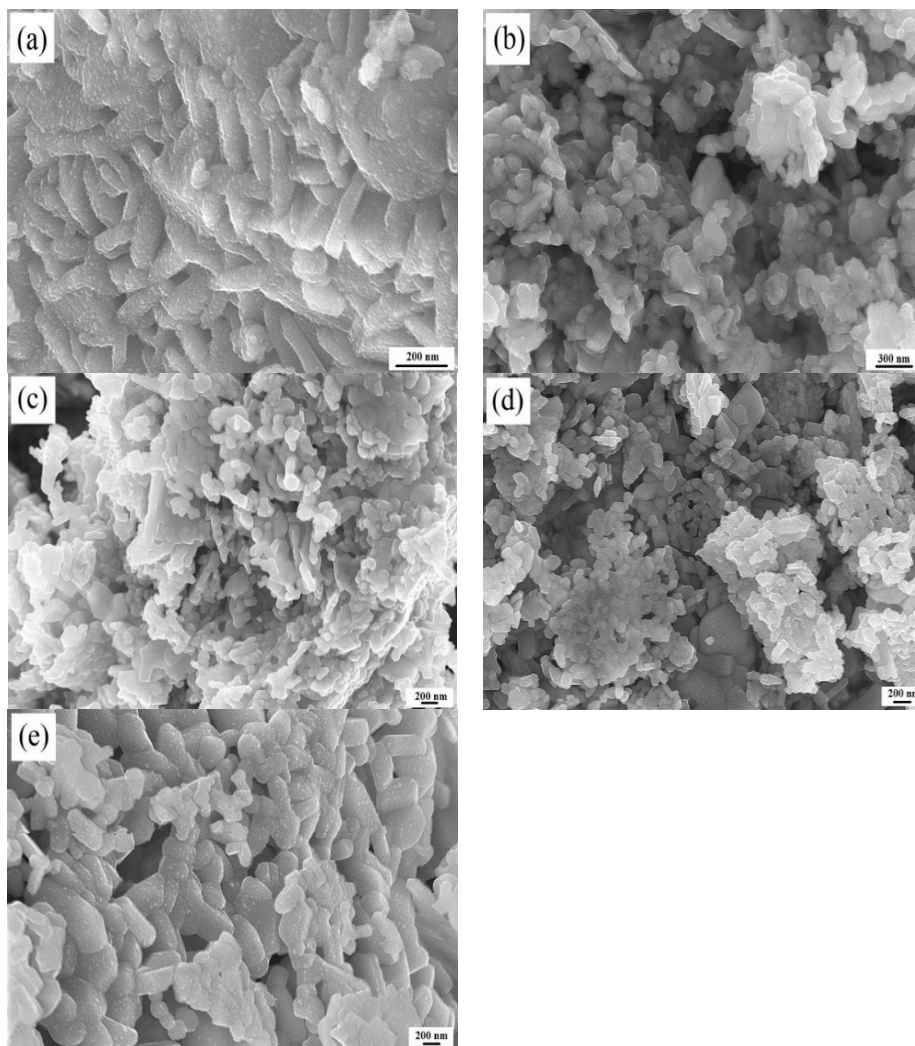


Figure 4. SEM images of products obtained at different annealing temperatures: (a) 700 °C; (b) 800 °C; (c) 900 °C; (d) 1000 °C; (e) 1100 °C.

The magnetic properties and crystallite size of samples as a function of temperature are summarized in Figure 5. The magnetic properties of samples increased significantly as the annealing temperature increased from 700 to 900 °C, with the highest M_s of 80.2 emu/g measured at 900 °C. Combined with the previous results, this may be ascribed to the reduction in the amount of residual nitrates, resulting in an increase in the proportion of $\text{SrFe}_{12}\text{O}_{19}$ present. Above 900 °C, the magnetic properties of the products deteriorated significantly as the annealing temperature increased. The changes in the magnetic properties can be explained by the changes in the sizes of the crystals (Figure 5b) and morphologies (Figure 4) of the samples. Excessive grain growth destroys the uniformity of samples, thus causing the deterioration of magnetic properties.

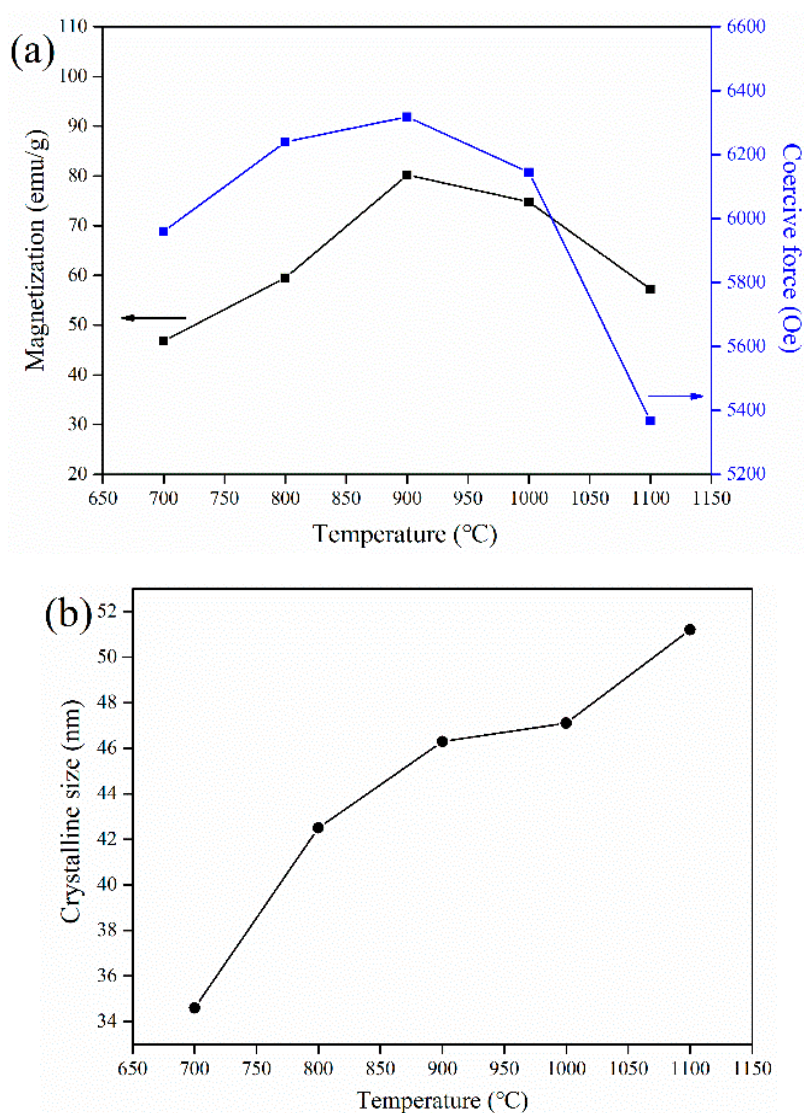


Figure 5. Effect of annealing temperature on the (a) magnetic properties and (b) crystalline size of the obtained SrFe₁₂O₁₉ powder.

3.2. Effect of Fe/Sr Molar Ratio

Previous studies have shown that an appropriate Fe/Sr molar ratio is one of the decisive factors for obtaining products with a single SrFe₁₂O₁₉ phase [33]. In the hydrothermal synthesis of SrFe₁₂O₁₉, Malick et al. [34] found that products with a single SrFe₁₂O₁₉ phase can be obtained at a specified Fe/Sr molar ratio. According to the studies of Hessian et al. on the preparation of SrFe₁₂O₁₉ via the co-precipitation method [5], the pure SrFe₁₂O₁₉ phase can be obtained at a Fe/Sr molar ratio of 9.23 and an annealing temperature of 900 °C. Wang et al. [35] prepared SrFe₁₂O₁₉ powder by using the sol-gel method, and found that the pure SrFe₁₂O₁₉ phase can be obtained at a Fe/Sr molar ratio of 11.5 and an annealing temperature of 800 °C.

Thus, to obtain products with a single SrFe₁₂O₁₉ phase, a series of experiments were performed by varying the Fe/Sr molar ratio from 11.6 to 11.8. Figure 6 shows the XRD patterns of products with an Fe/Sr molar ratio of 11.8 and annealed at different temperatures. The results of other analyses that were performed at the same time, including the phase content, crystalline size, and magnetic properties, are summarized in Table 2. These results indicate that the content of the α -Fe₂O₃ phase in the sample decreases as the annealing temperature increases. However, even at 1100 °C, it is not possible to obtain a product consisting of a single SrFe₁₂O₁₉ phase.

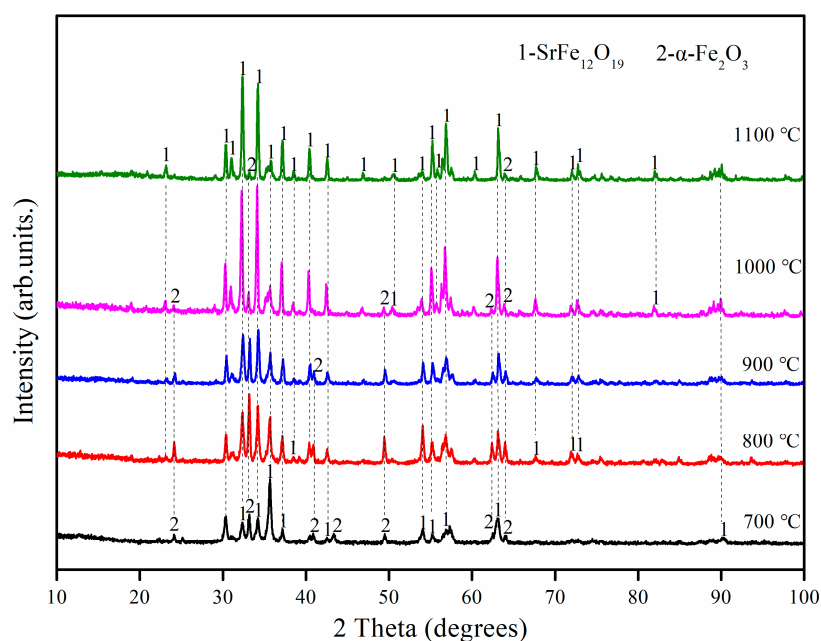


Figure 6. XRD patterns of $\text{SrFe}_{12}\text{O}_{19}$ with an Fe/Sr molar ratio of 11.8 and annealed at different temperatures.

Table 2. Effect of annealing temperature on the phase content, crystalline size, and magnetic properties of the obtained $\text{SrFe}_{12}\text{O}_{19}$ samples with an Fe/Sr molar ratio of 11.8.

Annealing Temperature (°C)	Phase Content	Crystalline Size (nm)	Magnetic Properties		
			M_s (emu/g)	M_r (emu/g)	H_c (Oe)
700	73% $\text{SrFe}_{12}\text{O}_{19}$ 27% $\alpha\text{-Fe}_2\text{O}_3$	29.6	40.8 ± 0.1	21.3 ± 0.1	854 ± 70
800	80% $\text{SrFe}_{12}\text{O}_{19}$ 20% $\alpha\text{-Fe}_2\text{O}_3$	30.2	42.7 ± 0.1	21.8 ± 0.1	4770 ± 50
900	86% $\text{SrFe}_{12}\text{O}_{19}$ 14% $\alpha\text{-Fe}_2\text{O}_3$	34.6	46.9 ± 0.1	24.2 ± 0.1	5260 ± 50
1000	92% $\text{SrFe}_{12}\text{O}_{19}$ 8% $\alpha\text{-Fe}_2\text{O}_3$	44.6	59.8 ± 0.1	31.1 ± 0.1	5080 ± 40

Moreover, the magnetic properties of the products listed in Table 2 increased significantly with an increase in the annealing temperature. This is mainly attributed to the increase of the $\text{SrFe}_{12}\text{O}_{19}$ phase content of the product.

Figure 7 and Table 3 present the XRD patterns of products with an Fe/Sr molar ratio of 11.4 and annealed at different temperatures. The $\text{SrFe}_{12}\text{O}_{19}$ powder samples obtained below 1000 °C contained some of the peaks associated with the $\alpha\text{-Fe}_2\text{O}_3$ phase (7–15%). At 1000 °C, products with a well-crystallized single $\text{SrFe}_{12}\text{O}_{19}$ phase were obtained. Moreover, the results in Table 3 show that the magnetic properties of products increased by increasing the annealing temperature. This is attributed to an increase in the $\text{SrFe}_{12}\text{O}_{19}$ phase content in the product.

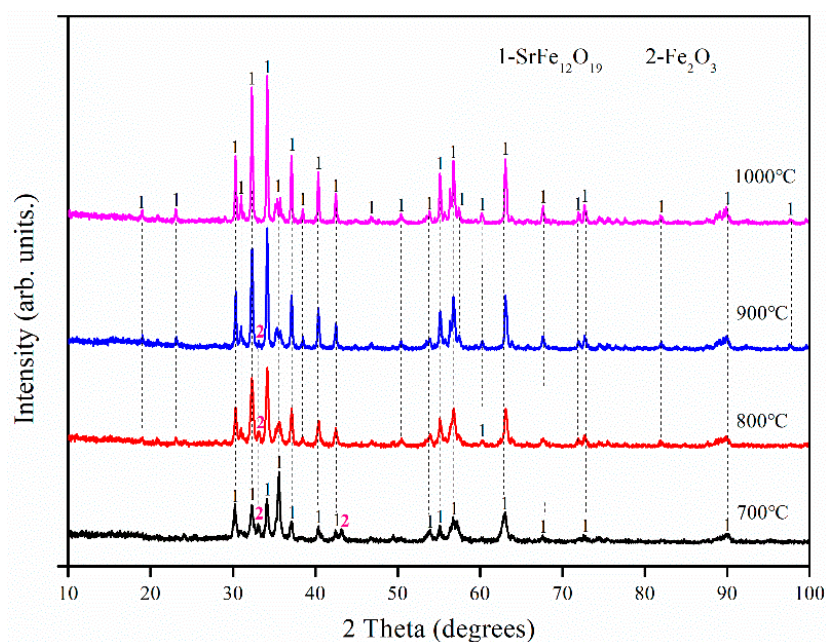


Figure 7. XRD patterns of $\text{SrFe}_{12}\text{O}_{19}$ with an Fe/Sr molar ratio of 11.6 by varying the annealing temperature.

Table 3. Effect of annealing temperature on the phase content, crystalline size, and magnetic properties of $\text{SrFe}_{12}\text{O}_{19}$ samples obtained with an Fe/Sr molar ratio of 11.6.

Annealing Temperature (°C)	Phase Content	Crystalline Size (nm)	Magnetic Properties		
			Ms (emu/g)	Mr (emu/g)	Hc (Oe)
700	85% $\text{SrFe}_{12}\text{O}_{19}$ 15% $\alpha\text{-Fe}_2\text{O}_3$	45.5	45.5 ± 0.1	21.3 ± 0.1	1170.1 ± 60
800	90% $\text{SrFe}_{12}\text{O}_{19}$ 10% $\alpha\text{-Fe}_2\text{O}_3$	50.1	50.1 ± 0.1	26.6 ± 0.1	5737.9 ± 30
900	93% $\text{SrFe}_{12}\text{O}_{19}$ 7% $\alpha\text{-Fe}_2\text{O}_3$	58.1	58.1 ± 0.1	31.1 ± 0.1	6437.8 ± 20
1000	100% $\text{SrFe}_{12}\text{O}_{19}$	74.2	67.5 ± 0.1	36.1 ± 0.1	6176.0 ± 20

3.3. Comparison of Magnetic Properties

To summarize, two of the samples exhibited improved magnetic properties. The first is the sample with an Fe/Sr molar ratio of 12 and annealed at 900 °C, which was named $\text{SrFe}_{12}\text{O}_{19}@900$. The other is the sample with an Fe/Sr molar ratio of 11.6 and annealed at 1000 °C, which was named $\text{SrFe}_{11.6}\text{O}_{19}@1000$. These two samples were compared with those prepared from chemicals/analytical chemicals reported in the literature. The results of this comparison are presented in Table 4.

Table 4. Performance comparison between the samples obtained in this study and those reported in the literature.

Sample	Synthetic Method	Magnetic Properties		
		Ms (emu/g)	Mr (emu/g)	Hc (Oe)
SrFe ₁₂ O ₁₉ @900	CPM	80.2	39.8	6318
SrFe _{11.6} O ₁₉ @1000	CPM	67.5	36.1	6176
SrFe ₁₂ O ₁₉ powder [20]	MA-SGM	54.8	29.5	5261
Sr _{0.9} La _{0.1} Fe _{11.9} Co _{0.1} O ₁₉ powder [20]	SGM	73	36	7700
Sr _{0.85} Nd _{0.15} Fe ₁₂ O ₁₉ powder [21]	CPM	63	35.15	6885
SrFe ₁₂ O ₁₉ nanoribbons [22]	SAE	67.9	37.3	7310
SrFe ₁₂ O ₁₉ powder [23]	SGM	59.3	34.9	6725

CPM = citrate precursor method; SGM = sol-gel method; MA-SGM = microwave-assisted sol-gel method; SAE = solution assisted electrospinning.

Although the content of the SrFe₁₂O₁₉ phase in SrFe_{11.6}O₁₉@1000 (100%) was higher than that in SrFe₁₂O₁₉@900 (97.9%), the grain size of SrFe_{11.6}O₁₉@1000 (74.1 nm) was significantly larger than that of SrFe₁₂O₁₉@900 (49.7 nm). The excessive grain growth may be the main reason why the magnetic properties of SrFe_{11.6}O₁₉@1000 were inferior to those of SrFe₁₂O₁₉@900. Moreover, Ms and Mr of SrFe₁₂O₁₉@900 reached 80.2 emu/g and 6318 Oe, respectively. Moreover, the comparison clearly shows that the magnetic properties of SrFe₁₂O₁₉@900 are competitive compared with those reported in the literature.

4. Conclusions

Using oily CRM sludge as an iron resource, nano-SrFe₁₂O₁₉ was synthesized successfully by using the citrate precursor method. The results showed that single-phase SrFe₁₂O₁₉ powder samples were obtained by decreasing the Fe/Sr molar ratio from the stoichiometric value of 12 to 11.6 and by increasing the annealing temperature to 1000 °C. An Fe/Sr molar ratio of 12 and annealing temperature of 900 °C produced nano-SrFe₁₂O₁₉ powder with a particle size of approximately 200 nm, and good magnetic properties (Ms 80.2 emu/g and Hc 6318 Oe), which are comparable to those of SrFe₁₂O₁₉ prepared from chemically pure materials.

Author Contributions: B.L. and S.Z. designed the experiments; B.L. performed the experiments, analyzed the results, and structured the manuscript; B.-M.S. and C.E. contributed with the discussions of experimental results. All authors contributed in the review of the manuscript.

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