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Large-scale production of strontium ferrite by molten-salt-assisted coprecipitation

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ABSTRACT

Large-scale production of strontium hexaferrite ($SrFe_{12}O_{19}$) particles was successfully achieved by molten-salt-assisted coprecipitation. A mixture of sodium hydroxide and sodium carbonate was served as mixed precipitant to obtain ferrite precursors. The effects of the Fe^{3+}/Sr^{2+} molar ratio, calcination temperature, calcination time, and molten-salt amount on the formation, morphology and magnetic properties of $SrFe_{12}O_{19}$ particles were investigated. The resultant particles were characterized by Fourier transform infrared spectroscopy, thermogravimetric analysis, X-ray diffraction, scanning electron microscopy, and vibrating sample magnetometer. Single-phase $SrFe_{12}O_{19}$ particles, with particle sizes of 0.8–1.2 μm, were obtained from the precursor (with a Fe^{3+}/Sr^{2+} molar ratio of 10) being calcined at 950 °C for 2 h using the mass ratio (NaCl to precursor) of 0.3. The saturation magnetization, remanent magnetization and coercivity were about 62 emu/g, 37 emu/g, and 4310 Oe, respectively. A comparison of the products obtained at different preparation-scales was also done. The results showed that it was easier to control the particle morphology using molten salt synthesis and more economical on a large-scale production.

1. Introduction

Hexagonal ferrites of magnetoplumbite structure with general formula $MFe_{12}O_{19}$ (M = Sr, Ba, Pb) have received wide recognition due to the abundance of required raw materials, low price and high stability. Strontium ferrite ($SrFe_{12}O_{19}$), as an important member of hexaferrites, has higher saturation magnetization, coercivity and the Curie temperature because of high magnetocrystalline anisotropy compared to barium ferrite ($BaFe_{12}O_{19}$) [1–3]. Furthermore, it shows excellent chemical stability and corrosion resistance. Due to these unique physical and chemical properties, $SrFe_{12}O_{19}$ is more popular than $BaFe_{12}O_{19}$ and has been applied widely in various fields, especially in modern permanent magnetic materials [4,5], magnetic recording media [6], microwave devices [7], magnetic fluids [8], magnetic coatings [9] and magnetic catalysts [10,11].

Traditionally, $SrFe_{12}O_{19}$ particles were prepared using the solid-state reaction method that involves annealing a mixture of $SrCO_3$ and Fe_2O_3 at high temperatures (>1200 °C) [12,13]. However, this method often introduces irregularity in particle shapes, defects in crystal structure and chemical inhomogeneity during ball milling. To overcome these disadvantages, numerous nonconventional synthetic routes have been developed including sol–gel processing [14], hydrothermal reaction [15], coprecipitation [16,17], microemulsion method [18,19], sonochemical method [20], glass-ceramic processing [21], spray pyrolysis [22], pulsed laser ablation [23] and so on. Among these routes, coprecipitation with simple process is economical and environmentally friendly because it involves inexpensive and less toxic iron salts and a reduced amount of organic solvent. For this reason, it is a method most suitable for mass production. However, one of the major difficulties encountered in the preparation of $SrFe_{12}O_{19}$ by coprecipitation is the relatively high solubility of $Sr(OH)_2$ in an aqueous solution when NaOH is used as a precipitant. Although excess strontium can be introduced in the starting composition, this solubility poses problems in maintaining the stoichiometry of $SrFe_{12}O_{19}$ [24]. To solve this problem, a mixture of NaOH and Na_2CO_3 was served as the precipitant to completely precipitate the ferrite precursor in our work. In addition, for improving homogeneity, molten salt synthesis was adopted in the preparation of $SrFe_{12}O_{19}$, which was based on the use of a salt with low melting point (such as alkali chlorides, sulfates, carbonates, or hydroxides) as a reaction medium during calcination process. The principles were stated in detail by relevant literatures [25–28], but the effects of molten-salt amount on the morphology and magnetic properties of $SrFe_{12}O_{19}$ particles were not discussed in earlier reports.

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There are many studies reported on $SrFe_{12}O_{19}$ since it is a very structure-sensitive material whose properties severely depend on differences in the preparation process. For example, Hessien et al. [29] systematically studied the effects of the Fe^{3+}/Sr^{2+} molar ratio, annealing temperature and pH on the formation, crystalline size, morphology and magnetic properties of $SrFe_{12}O_{19}$ nanoparticles. Lu et al. [30] investigated the influence of surfactants on the properties of the particles in detail. Furthermore, chromium substituted strontium ferrites were synthesized and the influence of inorganic template agents on their structural, optical, magnetic properties as well as their morphology was studied by Singhal et al. [31]. However, most of these studies were at small scales and there were few reports on a large-scale production of $SrFe_{12}O_{19}$ particles.

In this study, $SrFe_{12}O_{19}$ particles were synthesized economically utilizing industrial-grade raw materials through molten-salt-assisted coprecipitation on a large scale. That is, the ferrite precursors were obtained by coprecipitation method, and subsequently were calcined using molten salt synthesis to obtain strontium ferrite particles. The effects of the Fe^{3+}/Sr^{2+} molar ratio, calcination temperature, calcination time and molten-salt amount on the properties of $SrFe_{12}O_{19}$ particles were investigated to acquire the optimal conditions in the manufacturing process. The morphology, crystalline structure and magnetic properties were characterized. A comparison of $SrFe_{12}O_{19}$ particles obtained on different preparation-scales was also done. Such a study is intended to provide a facile and economic method for the mass production of $SrFe_{12}O_{19}$ particles.

2. Experimental

2.1. Materials and reagents

Analytical grade hydrochloric acid (HCl) from the SCRC (Sinopharm Chemical Reagent Co., Ltd.) was used. Iron (III) chloride ($FeCl_3$), strontium chloride ($SrCl_2$), sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3) and sodium chloride (NaCl) were all industrial-grade and used without further purification.

2.2. Apparatus

A schematic diagram of the apparatus used for the preparation of ferrite precursors is shown in Fig. 1. The main component of the apparatus was a stirred reactor (R) with a volume of 50 L. The aqueous solution of metal salts and mixed alkaline solution in feed vessels (V) were fed into the stirred reactor through feed pumps (P). Flow meters (F) were used to control and measure the flow of feeds. The mixed solution in the stirred reactor was stirred vigorously by the agitator (A). Control box (C) was used to control heating and the agitator. After coprecipitation, diluted hydrochloric acid was added into the stirred reactor from elevated tank (T) to adjust the pH.

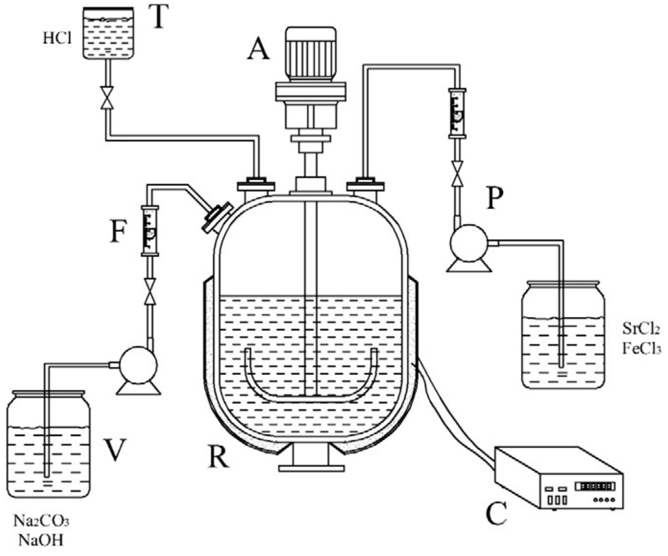

Fig. 1. Apparatus used for the preparation of ferrite precursor (stirred reactor (R), flow meter (F), control box (C), feed pump (P), agitator (A), feed vessel (V), and elevated tank (T)).

2.3. Preparation of $SrFe_{12}O_{19}$ on a large scale

The ferrite precursor was prepared by coprecipitation on a large scale. Firstly, $FeCl_3$ (1.54 M) and $SrCl_2$ (concentration varied along with Fe^{3+}/Sr^{2+} molar ratios) were dissolved in 18 L water with various Fe^{3+}/Sr^{2+} molar ratios (12, 11, 10, and 9.23). A Fe^{3+}/Sr^{2+} molar ratio of 9.23 was proposed by Hessien et al. [29] for this process. The aqueous solution of metal salts was precipitated with 18 L alkaline solution of NaOH (5 M) and Na_2CO_3 (0.16 M) to obtain ferrite precursor. The reaction equation during coprecipitation is shown as Eq. (1):

$$FeCl_3 + SrCl_2 + 3NaOH + Na_2CO_3 = Fe(OH)_3\downarrow + SrCO_3\downarrow + 5NaCl \tag{1}$$

The coprecipitation process was carried out under vigorous stirring (about 1000 rpm) at room temperature for 30 min. Then the aqueous suspension was stirred gently (about 500 rpm), heated to 80 °C and kept at this temperature for 1 h.

The colloid precipitate formed under extreme alkalinity showed difficulty in filtering and washing. Therefore, diluted hydrochloric acid was added to neutralize the aqueous suspension. A plate-and-frame press process filtered off the reddish brown precipitate to obtain the precursor. Then the precursor was put in a shallow plate and dried at 110 °C for 48 h in air. The dried precursor particles were ground with various amounts of NaCl salt through a three-roll grinder (S65, Dongfang Huayang Machinery Factory, Changzhou). The mass ratio of NaCl to the precursor was defined here as *R*, where *R* was 0, 0.2, 0.3 and 0.4, respectively. After sufficient grinding, the mixtures of NaCl salt and the precursor were calcined at rate of 10 °C/min in a static air atmosphere up to different temperatures (900 °C, 950 °C, and 1000 °C), held at this temperature for various sintering times (1 h, 2 h, and 3 h) and subsequently cooled naturally to room temperature. The assumptive main reaction mechanism of thermal decomposition is listed as follows:

$$2Fe(OH)_3 \overset{\Delta}{=} Fe_2O_3 + 3H_2O \tag{2}$$

$$SrCO_3 \overset{\Delta}{=} SrO + CO_2\uparrow \tag{3}$$

$$6Fe_2O_3 + SrO \overset{\Delta}{=} SrFe_{12}O_{19} \tag{4}$$

The calcined powders were washed with water to remove the residual salt and dried at 110 °C in air for about 24 h. There were four parameters investigated to obtain the optimal conditions in the manufacturing process (see Table 1).

Table 1
The main parameters in the manufacturing process.

Parameters	Level			
Fe^{3+}/Sr^{2+} molar ratio	12	11	10	9.23
Calcination temperature (°C)	900	950	1000	
Calcination time (h)	1	2	3	
Mass ratio *R* (NaCl to precursor)	0	0.2	0.3	0.4