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Current Perspectives

Mechanism and microstructural evolution of polyol mediated synthesis of nanostructured M-type $SrFe_{12}O_{19}$

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ABSTRACT

The synthesis mechanism of nanostructured M-type strontium hexaferrite $SrFe_{12}O_{19}$ with high coercivity (5.7 kOe) obtained by a polyol process and annealing is proposed. The results show that the hexaferrite is synthesized through the formation of a complex with diethylene glycol during the hydrolysis and solvation stage, followed by the condensation of magnetite and strontium oxide. The results of the monitoring of the process by X-ray diffraction (XRD) of synthesized powders, magnetization hysteresis loops and micromorphology are presented and discussed. The proposed mechanism suggests the intermediate formation of the magnetite phase, which shows coercivity near zero at room temperature and confirms the nanoscale of the particles. Results of thermogravimetric and differential thermal analysis indicate that this phase is followed by the formation of the hematite phase after a heat treatment up to 543 °C in an oxidizing atmosphere. Finally, the hexagonal phase is obtained after application of annealing at 836 °C through the reaction between hematite and strontium oxide.

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1. Introduction

M-type hexaferrites, Sr-hexaferrites in particular, have been the subject of interest among many researchers owing to their appropriate magnetic properties, chemical stability and low cost compared with magnetic rare-earth compounds since their discovery by Philips in the 1950s [1,2]. Owing to their unique physical and chemical properties, $SrFe_{12}O_{19}$ is more popular than $BaFe_{12}O_{19}$, and it has been widely applied in various fields, especially in modern permanent magnetic materials [3], magnetic hyperthermia [4], hybrid photocatalysts [5], loudspeakers, permanent magnetic motors, many-coil instruments (galvanometers, voltmeters and ammeters) and microphones [6].

Sr-hexaferrites have been synthesized by various methods [7], such as the co-precipitation method [8], pulsed laser deposition (PLD) technique [9], microwave-assisted [10] Pechini method [11], and ceramic sintering with a heat treatment at 1400 °C [12], with the recent focus on obtaining nanoparticles [13,14]. Even though, $SrFe_{12}O_{19}$ has not been obtained by polyol, it is known that polyol method has been well accepted because of its simplicity and its advantages, the synthesis by polyol provide the possibility to control the kinetics of experimental conditions and that these are easily to scale-up [15]. Additionally it is know that the obtained powders show homogenous phase composition, narrow particle distribution and high specific area [16].

$SrFe_{12}O_{19}$ has excellent characteristics because it is a typical magnetoplumbite type of hexagonal ferrite [1]. As is shown in Fig. 1, Sr-hexaferrite is built up from smaller units including a cubic block S, with a spinel-type structure and a hexagonal block R containing the Sr^{2+} ions. The hexagonal Sr-ferrite has 24 magnetic Fe^{3+} ions per unit cell, which are distributed on five different crystallographic sites; three octahedral sites, 12k, 2a and $4f_2$; one tetrahedral site, $4f_1$; and one trigonal bi-pyramidal site, 2b [17]. Among them, 12 Fe^{+3} ions have a chemical function, with four of them having spin in the downward direction at $4f_1$ ($2Fe^{3+}$) and $4f_2$ ($2Fe^{3+}$) and the other 8 Fe^{+3} ions having spin in the upward direction at 12 k ($6Fe^{3+}$), 2a ($1Fe^{3+}$) and 2b ($1Fe^{3+}$) [18]. Owing to its complicated crystal structure, its synthesis represents a major challenge regardless of the method chosen.

Polyol synthesis was originally introduced by Fievet et al. [19] as an excellent method for the synthesis of nanoparticles from metallic salts by using a poly-alcohol, which act as amphiprotic solvents, as well as complexing, reducing and surfactant agents, depending on the studied system. Hydrolysis and reduction reactions can be performed in these liquids, allowing the production of a wide variety of size- and shape-controlled inorganic

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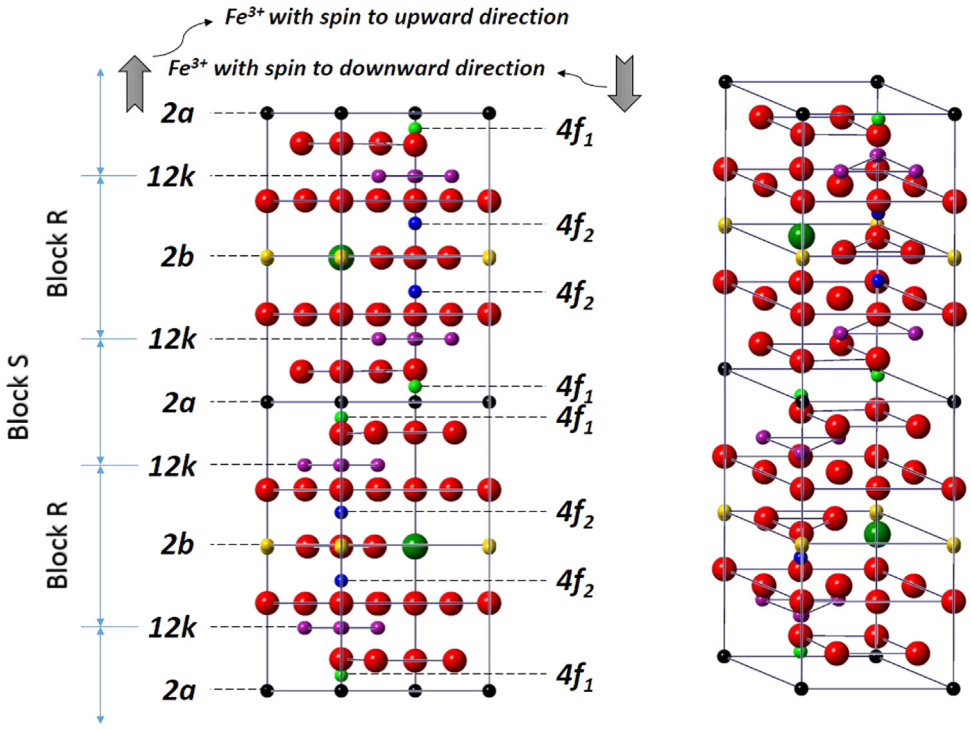

Fig. 1. Interstitial sites in the strontium hexaferrite crystal cell. Large red circles are O^{2-}, large green circles are Sr^{2+}, and small circles with different colors represent Fe^{3+} in its interstitial positions.

nanoparticles [20–22]. However, the reaction mechanism for the synthesis of hexagonal ferrite by polyol has not yet been described. The poly-alcohols used in this process are ethylene glycol (EG), diethylene glycol (DEG), 1,2-propanediol, tetra-ethylene glycol and glycerol [23–24]. This process is heralded for its self-seeding mechanism and lack of required "hard" or "soft" templating materials, making it an ideal process for industrial scale-up owing to the low cost of processing [25].

In this work, the synthesis of nano-crystalline strontium hexaferrite has been achieved by complexing strontium and iron ions with diethylene glycol, followed by annealing at temperatures as low as 750 °C. We increased the annealing temperature until a value near to conventional method to evaluate the effect of particle size on the coercive field. Moreover, a mechanism for the synthesis of hexaferrite by this method is proposed, which can be applied to similar systems. The obtained hexaferrite has adequate magnetic properties to be applied as a permanent magnetic material.

2. Experimental part

Stoichiometric amounts of $(C_2H_3O_2)_2Sr$ (purity 99.995% Sigma Aldrich, Ac_2Sr) and $(C_2H_3O_2)_2Fe$ (purity 99.8% Sigma Aldrich, Ac_2Fe) were dissolved in 125 mL of diethylene glycol ($C_4H_{10}O_3$, purity 99.8% Sigma Aldrich) to obtain $SrFe_{12}O_{19}$ to achieve the synthesis of hexaferrite according to the following equations:

$$(C_2H_3O_2)_2Sr + 12(C_2H_3O_2)_2Fe + 13H_2O + 3O_2 \xrightarrow{\Delta, DEG, H_2O} SrFe_{12}O_{19} + 26C_2H_4O_2 \quad (1)$$

Ac_2Fe was used as precursor owing to Fe^{2+} being completely soluble in a mixture of DEG with water, whereas Fe^{3+} is insoluble in the same medium. A controlled quantity of water was used to promote the hydrolysis of metals owing to dissociation of water, which is necessary for synthesizing oxides [19–21]. The solution was then brought to boiling (240 °C) under mechanical stirring using a heating rate of 10 °C/min. The solution was maintained at boiling temperature in reflux for 5 h. Once cooled, the powders were collected by means of three washing cycles consisting of the following: suspension in ethanol, centrifugation at 12,000 rpm for 15 min, and finally drying at 80 °C in air. At this point the powders were named "as obtained." After that, the powders were annealed at different temperatures from 750 to 1050 °C in air, in order to study the annealing temperature in the crystal structure and magnetic properties.

The obtained powders were characterized by X-ray diffraction (XRD) using an Inel Equinox 2000 diffractometer with $CoK_{\alpha 1}$ ($\lambda = 1.7890100$ Å) radiation. Patterns were collected in a 2θ interval of 20–85° with increments of 0.02. Rietveld refinements were performed on the X-ray diffraction patterns to obtain the percentages of different phases, crystallite sizes and microstrains of the powders. This method considers all collected information in a diffraction pattern and uses a least-squares approach to refine the theoretical line profile until it matches the measured profile [26]. Crystallographic data were obtained from the Crystallography Open Database (COD) [27]. Scanning electron microscopy (SEM) using a JEOL-100-CX II helped determine the morphology and qualitative particle size. Magnetization studies were carried out at room temperature using a MicroSense EV7 vibrating sample magnetometer (VSM) with a maximum field of $\pm$ 18 kOe.

The stabilities of the synthesized powders were measured by studying their thermal behaviors in a thermogravimetric analyzer (TGA/SDTA 851e Mettler-Toledo). The experiments were performed with a heating rate of 10 K min^{-1} using an air flow of 6×10^{-3} m^3 s^{-1}.

3. Results and discussion

In Fig. 2, the X-ray diffraction pattern of the obtained powder from the polyol process without post-treatment is presented. As can be observed, there are only peaks corresponding to the spinel

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