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Synthesis of M-type $SrFe_{12}O_{19}$ by mechanosynthesis assisted by spark plasma sintering

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ABSTRACT

We present a comparative study of synthesis of M-type strontium hexaferrite from strontium and iron single oxides mechanically activated by high-energy ball milling for 5 h, and assisted by two different methods: (a) conventional heat treatment and (b) Spark Plasma Sintering (SPS), both at relative low temperatures (⩽900 °C). Although it was found that both methods promoted the complete structural transformation of precursors to Sr-hexaferrite phase (S.G. *Pmc21*) for temperatures above 700 °C, higher saturation magnetization was found for SPS samples. X-ray diffraction analysis revealed that the structural transformation undergoes formation of an intermediate metastable structure ($Fe_2Sr_2O_5$) in both methods, but with slight different kinetics. Maximum specific magnetization of 67 emu/g at 18 kOe and coercivity of 3.7 kOe were recorded from powder mixtures milled for 5 h, which were subsequently SPS-ed at 700 °C. By contrast, although magnetization values for the same milled samples after being annealed at 700 °C slightly decreased, it leads to a significant increase in the coercive field reaching 5.4 kOe. These results are explained on the basis of factors such as the complete formation of hexaferrite and the attained density of consolidated powders, in addition to particle and grain sizes also reported.

1. Introduction

M-type hexagonal ferrites have been extensively used as permanent magnets, high-density magnetic recording media [1] for the last decades and are currently used in microwave devices working at frequencies in the gigahertz range [2]. Although many other hard magnetic materials have been developed after these years, the hexaferrite performance/cost ratio is still extremely favorable. The unit cell of these of ferrites consists of a spinel block (S) with two layers of four oxygen atoms with three divalent metal ions between each layer in four octahedral sites, where the cation is surrounded by six oxygen anions and two tetrahedral sites where four oxygen anions surround the cations; and a block (R) (with the stoichiometry $(SrFe_6O_{11})^{-2}$) with three hexagonally packed layers of four oxygen atoms each, but one of the oxygen atoms in the center layer is replaced by a similarly sized divalent metal atom with an overlap of hexagonally and cubically packed layers [3].

Among these ferrites, strontium hexagonal ferrite, with strontium as divalent metal ion, $SrFe_{12}O_{19}$, possesses a special place due to its magnetic properties and particularly due to its larger magnetocrystalline anisotropy [4].

Hexaferrites can be synthesized by several processes. The conventional and oldest one is by calcination and sintering of a mixture of oxides or carbonates in a furnace at 1300 °C [5]. This process produces large particles and consumes extensive energy. Nanostructured hexaferrites can be produced by different methods such as sol–gel [6,7], hydrothermal [8], coprecipitation [9], spray-drying and microemulsion [10], conventional route [11] among others [12,13]. A particular method is mechanosynthesis; typically this method promotes formation of ferrites by mechanical activation of carbonate strontium and iron oxide [13,14]. In comparison with the traditional method (solid state reaction) [15], the mechanochemical method has demonstrated to achieve high coercivity and magnetic saturation in these materials [11–16], nevertheless the mechanosynthesis is a potential process for mass production.

Luo [14] prepared strontium hexaferrite by mechanosynthesis of a mixture of $SrCO_3$ and Fe_2O_3 with subsequent annealing. They obtained an amorphous material after ball-milling for 30 h, and a $SrFe_{12}O_{19}$ single phase after annealing at 900 °C for 2 h. The attained saturation magnetization reached 58.2 A m^2/kg (58 emu/g), whereas the coercivity was 281.2 kA/m (3500 Oe) at room temperature. A similar study using the mechanosynthesis

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route was reported by Sharma et al. [16] to obtain barium hexaferrite. By setting up the same experimental parameters they reported certain enhancement in some magnetic properties; such as the saturation magnetization and coercivity. Other authors like Ketov et al. [17] studied the effect of mechanochemical treatment and subsequent annealing of $SrFe_{12}O_{19}$ powders. From their results it can be inferred that even when the milling action cause deterioration on the magnetic properties, the annealing process led to a sharp improvement of them, due to crystallization and formation of the $SrFe_{12}O_{19}$ phase with fine crystallites. The best magnetic properties achieved for the milled hexaferrite were reached ($\mu_0 H_{ci} \approx 0.42$ T, $B_r \approx 0.24$ T and $(BH)_{max} \approx 9.6$ kJ/m^3) after the milling and annealing actions of the powder at 950–1000 °C for 1 h. In this case, the average particle size was about 1 μm and the average crystallite size was 100–200 nm.

Although there is a great number of published works in the magnetic materials processing via the mechanosynthesis technique, and thus showing its technological importance, this technique itself seems not to provide enough energy as to promote the complete formation of hexaferrite, even when using long milling times. It is for this reason that a post-heat treatment must be applied to the milled powder to complete formation of the strontium hexaferrite. Thus, one approach to succeed in this task is to apply annealing temperatures larger than 750 °C, although it leads to an increase in the particle size. In order to find out technical alternatives to synthesize and sinter strontium hexaferrite, with no substantial grain growing [17], we propose to apply the Spark Plasma Sintering (SPS) technique to the oxide powder mixtures ball milled for 5 h. The SPS process is known as a conveniently superfast and low temperature route not only useful to consolidate, but also to promote the chemical reaction of nanoparticles. Briefly, in the SPS method [19], the sample (usually powder) is compressed into a graphite dies matrix while operated in vacuum conditions and high intensity electric pulses are supplied into the system. Electric current goes therefore through the die, which allows heating rates as high as 1000 °C/min. If the sample is a conductor, the electric flux goes also through the sample leading to a more efficient heating process. Recent experimental results show that in addition to the heating process, the electric flux promotes ionic diffusion in the sample, thus resulting in an enhanced sintering process. But even when the sample is a non-conductive electric material, it appears that the electric field can allow the diffusion processes [20]. Comparatively, the conventional heat treatment or annealing is a long time process, which is also based on atomic diffusion, but due to usually prolonged treating times, an increase in both particle and crystallite size is expected when used as a method for synthesize [21].

In this work, we compared two different processing routes for strontium hexaferrite, both starting from commercial oxides high-energy ball milled for 5 h. The first series of materials was conventionally annealed from 700 to 900 °C while the other, consisted of SPS-ed powder at temperatures as low as 700 °C. As it will be shown, both routes induced the complete formation of nanostructured strontium hexaferrites, but with different magnetic properties, as a consequence of the different particle size.

2. Experimental procedure

Fe_2O_3 (Sigma Aldrich, 99% purity) and calcinated SrO (Sigma Aldrich, 99.9% purity) powders were used as precursor materials. These powders were mixed in a stoichiometric ratio to obtain hexaferrite according to the following equation:

$$SrO + 6Fe_2O_3 \rightarrow SrFe_{12}O_{19} \quad (1)$$

A total of 5 g of the starting mixtures were loaded with steel balls of 1.27 cm in diameter inside a steel cylindrical vial (50 cm^3) (steel/steel, S/S) at room temperature. The mixture was milled using a high-energy ball mill Spex 8000D to promote a mechanical activation of the sample. The milling time was set to 5 h in order to avoid the sample contamination from the milling medium [13]. The ball to powder weight ratio was 10:1. To prevent excessive heating of the vials, experiments were carried out by alternating 90 min of milling followed by 30 min in standby. All experiments were performed in argon at room temperature. After that, the milled powder (activated for 5 h) was post-treated in order to synthesized the strontium hexaferrite by following two routes: (a) compaction at 800 MPa and annealing from 500 to 900 °C for 2 h in air atmosphere, using a tube furnace and (b) SPS at different temperatures with a heating rate of 100 °C/min using a Dr. Sinter 1050 apparatus, applying pressure of 635 MPa and 6×10^{-2} Pa vacuum, setting holding times at 500, 600, 700, 800 and 900 °C for 10 min.

All the obtained compacts were characterized by X-ray diffraction (XRD) using an Equinox 3000 equipped with a multichannel detector (X'celerator) and by using Co Kα_1 ($\lambda = 1.7854003$ Å) radiation. Patterns were collected in a 2θ interval of 20–85° with increments of 0.03 (2θ). A qualitatively particle size analysis was performed by using a scanning electron microscopy (SEM) JEOL JSM 6300.

Magnetization studies were carried out at room temperature using a MicroSense EV7 vibrating sample magnetometer The coercivity (H_c), specific magnetization (M) and magnetic polarization (J) data were measured, with a maximum applied field of 18 kOe (1400 kA/m).

3. Results and discussion

3.1. Characterization of the crystalline structure

Fig. 1 shows the X-ray diffraction (XRD) pattern of stoichiometric mixtures milled for 5 h and annealed at different temperatures, from 500 to 900 °C. The XRD pattern corresponding to the mixture of powders as-milled for 5 h (Fig. 1), exclusively shows peaks of Fe_2O_3 (ICSD 22505, *R3cH*). SrO diffraction peaks are not apparent in XRD patterns because of stoichiometry, Sr concentration is 12 times smaller than that of Fe, and in this figure, the whole diffraction pattern is strongly compressed. Crystallite sizes calculated for as milled powders are around 29.4 nm, confirmed by the wider peaks on XRD pattern.

An increase in grain sizes was calculated after annealing temperature of 600 °C up to 39.5 nm and an increase in microstrain up to 0.0014. This increase in microstrain could indicate proximity of a phase change. At this temperature, it is interesting to remark the appearance of a new peak at 33.9° of 2-theta. This phase is identified as $Fe_2Sr_2O_5$ (ICSD 66403, *Ibm2*) which is a metastable structure between Fe_2O_3 and hexaferrite that acts as a nucleation site for the formation of hexaferrite. At temperatures between 600 and 700 °C new peaks corresponding to the hexaferrite are detected ($SrFe_{12}O_{19}$, ICSD 16158, *P63mmc*), but peaks corresponding to hematite still remain, indicating that the reaction has not been completed.

At 700 °C microstrain still increases for hematite structure, a value of 0.0032 is achieved, but hexaferrite structure starts to

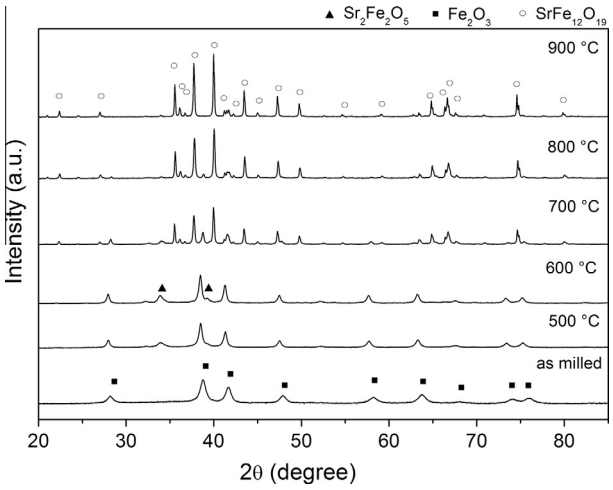

Fig. 1. X-ray powder diffraction patterns of mixture (Fe_2O_3 + SrO) milled for 5 h, pressed at 800 MPa and annealed at indicated temperatures, from 500 to 800 °C.