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Phase transformation of strontium hexagonal ferrite

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ABSTRACT

The phase transformation of strontium hexagonal ferrite ($SrFe_{12}O_{19}$) to magnetite (Fe_3O_4) as main phase and strontium carbonate ($SrCO_3$) as secondary phase is reported here. $SrFe_{12}O_{19}$ powder was obtained by a heat treatment at 250 °C under controlled oxygen flow. It was observed that the phase transformation occurred when the $SrFe_{12}O_{19}$ ferrite was heated up to 625 °C in confinement conditions. This transformation took place by a combination of three factors: the presence of stresses in the crystal lattice of $SrFe_{12}O_{19}$ due to a low synthesis temperature, the reduction of Fe^{3+} to Fe^{2+} during the heating up to 625 °C, and the similarity of the coordination spheres of the iron atoms present in the S-block of $SrFe_{12}O_{19}$ and Fe_3O_4. X-ray diffraction analysis confirmed the existence of strain and crystal deformation in $SrFe_{12}O_{19}$ and the absence of them in the material after the phase transformation. Dispersive X-ray absorption spectroscopy and Fe^{57} Mössbauer spectroscopy provided evidences of the reduction of Fe^{3+} to Fe^{2+} in the $SrFe_{12}O_{19}$ crystal.

1. Introduction

The strontium hexagonal ferrite ($SrFe_{12}O_{19}$) has been extensively studied from the middle of XX century [1,2]. Due to its magnetic properties (uniaxial anisotropy and high magnetization) it has been used as a permanent magnet and as information storage media [3–7]. The ceramic method, the first method used to obtain $SrFe_{12}O_{19}$, requires heating up to 1200 °C [8]. In order to decrease the synthesis temperature, chemical methods, like sol–gel and co-precipitation have been developed. Such methods involve heat treatments between 800 °C and 1000 °C [9–18]. Moreover, some variations of these methods allow synthesizing hexagonal ferrites at temperatures below 500 °C [13,17,19].

$SrFe_{12}O_{19}$ synthesized at low temperatures has been extensively characterized structurally and magnetically, but there are few studies about the thermal stability of the obtained material [20]. Due to low temperature involved in the synthesis, the hexagonal ferrite could have crystal imperfections and some structural stresses. In our previous work we reported experimental evidence about the metastability of $SrFe_{12}O_{19}$ powder obtained at 400 °C under oxygen flow [21]. To our knowledge, there are no other reports on the subject.

The aim of this paper is to report the phase transformation of $SrFe_{12}O_{19}$ to magnetite (Fe_3O_4) and strontium carbonate ($SrCO_3$). The factors that promote this phase transformation were analyzed. Interestingly and by the first time to our knowledge, the Fe^{3+} to Fe^{2+} reduction in the $SrFe_{12}O_{19}$ crystal is reported here.

2. Materials and methods

The $SrFe_{12}O_{19}$ powder was obtained using the sol–gel method with organometallic hexaferrite as precursor [14,22]. For this purpose, a highly concentrated ferric nitrate solution with citric acid as the primary coordinator agent was prepared. In order to achieve the atomic ratio Fe/Sr = 12, a proper amount of $SrCO_3$ was added. After that, benzoic acid and ethylene glycol (secondary coordinators agents) were added. Then, the clear solution was slowly evaporated. During the process, NO_3 group was decomposed emitting nitrous gases (NO^- and NO_2). The thermal treatment produced the emission of CO^-, CO_2 and H_2O as well. The heating was maintained until the gel was dried forming a viscous residue. To obtain $SrFe_{12}O_{19}$, the dried gel (organometallic hexaferrite) was thermally treated for 3 h at 250 °C under an oxygen flow of 200 cm^3/min.

In order to induce the phase transformation of the $SrFe_{12}O_{19}$ a heat treatment was performed. The treatment was carried out

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from room temperature to 625 °C at a rate of 5 °C/min with the sample placed in a closed capsule of aluminum.

The study of the phase transformation was carried out with a combination of spectroscopic techniques. It is well known that X-ray absorption near edge structure technique is very sensitive to changes in oxidation state of the material under research. On the other hand, ^{57}Fe Mössbauer spectroscopy (MS) was employed to corroborate the degree of oxidation state of iron. Both techniques combined with X-ray diffraction (XRD) allow performing the accurate identification of iron oxide involved in the phase transformation. Furthermore, MS and magnetometry techniques contribute to the characterization of the magnetic phases involved in the process.

Structural properties of the powders used in this report were analyzed by XRD in a θ–2θ diffractometer (Rigaku D/max equipped with a vertical goniometer) using Cu–K_α radiation. The average crystallite size of the phases involved was calculated using the Scherrer equation [23], and the crystal lattice strains were determined through the Williamson–Hall method [24]. In order to determine the phases quantitatively, MAUD program [25] (based on the Rietveld method) was used. The calculated Rietveld reliability parameters were: S=2.2, R_w(%)=12.5, R_{wnb}(%)=12.3, R_b(%)=9.5, R_{exp}(%)=5.7 for XRD corresponding to as made sample, and S=2.1, R_w(%)=16.3, R_{wnb}(%)=15.7, R_b(%)=13.9, R_{exp}(%)=7.7 for XRD of the sample after the phase transformation.

MS at room temperature was applied under transmission geometry with a standard constant acceleration spectrometer using a 10 mCi ^{57}CoRh radioactive source. The isomer shifts were referred to α-Fe.

The measurement of mass magnetization as a function of applied magnetic field (σ vs. H) at 300 K, and mass magnetization as a function of temperature (σ vs. T) under ~7958 A/m applied magnetic field were performed using a commercial vibrating sample magnetometer.

The thermal analysis was carried out in a differential scanning calorimeter under dynamic Ar atmosphere. The heating was performed at 5 °C/min scan rate. The powder sample was placed in a closed aluminum paper and sealed in aluminum pan.

In situ X-ray absorption near edge structure (XANES) spectra at Fe K-edge were collected in transmission mode using the D06A-DXAS beamline at Laboratorio Nacional de Luz Síncrotron (LNLS), Campinas, Brazil. During the experiment the sample was placed in an oven applying 5 °C/min heating rate. The XANES data analysis was performed using *Athena* software by subtracting a linear background and rescaling the absorbance by normalizing the difference between the baseline and the post-edge absorption. The calibration of the energy scale was performed by measuring metallic foil of Fe. The sample for XANES experiments was prepared in the form of 5 mm-diameter pellet using standard pressure procedure. Boron nitride powder was mixed with previously sieved 10 μ-mesh powder of the sample under research. The mass of the powder was estimated to optimize the absorption jump.

3. Results and discussion

Fig. 1 shows the XRD patterns of powders corresponding to the sample before and after being submitted to the heating. As it can be seen from the XRD pattern of the sample before heating (as made sample), the crystalline planes corresponding to a hexagonal ferrite $SrFe_{12}O_{19}$ (S.G. $P_{63/mmc}$, sys. hexagonal, a=0.588 nm, c=2.304 nm [26]) as main phase, and $SrCO_3$ (S.G. R-3m, sys. rhombohedral, a=0.5092 nm, c=0.9530 nm [27]) and maghemite (γ-Fe_2O_3) (S.G. Fd-3m, sys. cubic, a=0.835 nm [28]) as secondary phases were identified (Fig. 1a). After heating up to 625 °C the phase transformation was corroborated. The peaks corresponding to the magnetite (Fe_3O_4) as main phase (S.G. Fd-3m, sys. cubic, a=0.8394 nm [29]) and $SrCO_3$ as secondary phase were found (Fig. 1b).

It is possible to emphasize that the composition of the as made sample determined by XRD (Fig. 1a) is closely related to the synthesis procedure used. Even though the thermal treatment under oxygen flow allows decreasing the temperature needed to obtain hexagonal ferrite $SrFe_{12}O_{19}$, the as made sample is a mix of phases. About 40% of the sample is formed by γ-Fe_2O_3 and $SrCO_3$. Both are the inorganic precursors of the hexagonal ferrite. Similar effects were observed when the method of synthesis was the traditional sol–gel (thermal treatment in air atmosphere) [30].

Following the traditional steps of the sol–gel method, a thermal treatment with temperatures between 1050–1100 °C is necessary to complete the transformation of the inorganic phase precursors (γ-Fe_2O_3 and $SrCO_3$) to hexagonal ferrite [14]. The more accurate reports indicate that the hexagonal ferrite begins to form between 550 °C and 600 °C [14,31] and the process is maximum over 780 °C [22]. When the traditional thermal treatment is used (in air atmosphere) the temperature necessary to obtain $SrFe_{12}O_{19}$ is high. This happens because the decomposition of the organic material leads to emission of CO_2 gas which recombines with Sr^{2+} to form

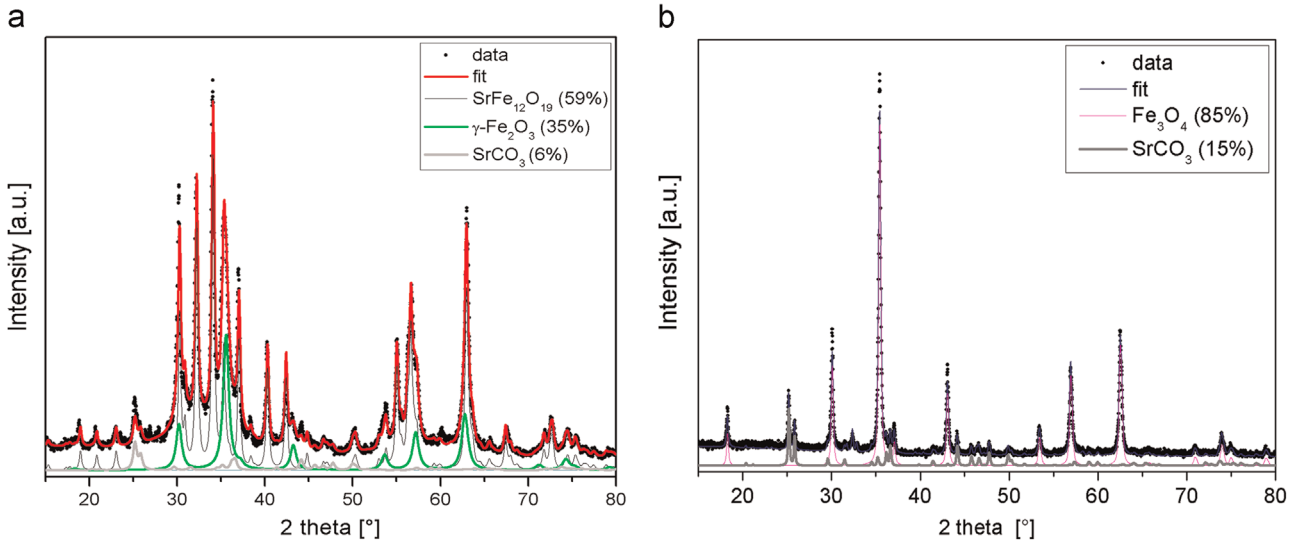

Fig. 1. XRD patterns: (a) as made sample before and (b) after its heating up to 625 °C.