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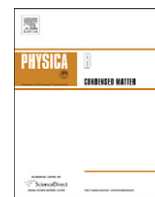


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Formation of a magnetic composite by reduction of Co-Nd doped strontium hexaferrite in a hydrogen gas flow

C.A. Herme^a, P.G. Bercoff^{b,*}, S.E. Jacobo^a

^a Facultad de Ingeniería, Universidad de Buenos Aires, LAFMACEL-INTECIN. Paseo Colón 850, 1063 Buenos Aires, Argentina

^b Facultad de Matemática, Astronomía y Física, Universidad Nacional de Córdoba. IFEG, CONICET. Ciudad Universitaria. 5000 Córdoba, Argentina

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ABSTRACT

Co-Nd strontium hexaferrite nanoparticles synthesized by the self-combustion method were treated in a hydrogen flow at different temperatures and times. The samples were characterized structurally by scanning electron microscopy and X-ray diffraction and magnetically with a vibrating sample magnetometer. Phase identification showed decomposition of the hexaferrite structure into Fe₃O₄ and different strontium mixed oxides. The sample treated at 500 °C for 30 minutes shows good magnetic properties due to the formation of a magnetite/hexaferrite composite. In this case magnetization is very close to the original sample while the coercivity slightly diminishes. The hexagonal phase is almost completely transformed into different oxides at a reducing temperature of 500 °C for 120 minutes. The obtained results are analyzed in terms of the phase composition and of the magnetic susceptibility of the studied samples.

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1. Introduction

Hexagonal ferrites have multiple commercial applications: magnetic recording, permanent magnets, microwave devices applications, ferrofluids, and many others. They are hard magnetic materials with a general formula $x\text{SrO} \cdot y\text{Fe}_2\text{O}_3 \cdot z\text{MeO}$, where Me is a divalent metal, structurally related with magnetoplumbite. Besides, they are characterized by their large magnetocrystalline anisotropy values.

In almost every case, the ion Sr²⁺ can be partially or totally replaced by Ca²⁺, Ba²⁺, Pb²⁺, or even La³⁺ (in such case an equivalent amount of Fe³⁺ should be replaced by Fe²⁺ or another divalent cation).

It is well known that the properties of any material can be successfully modified by thermal treatment in different gas atmospheres. New magnetic phases can be obtained in this way.

The reduction of iron oxides in hydrogen atmosphere has been widely studied and carries out an important role in many catalytic reactions: ammonia synthesis, carbon monoxide hydrogenation, etc. Great attention has been devoted to hematite reduction, Fe₂O₃, to magnetite, Fe₃O₄. The nature of this process is extremely complicated and depends on the physicochemical characteristics of the oxide and the reduction conditions. Some of the influential factors in this reduction process are the temperature, steam

pressure, particle size and the presence of impurities. It should not be ignored that such oxides are non-stoichiometric compounds, due to the easy tendency of Fe²⁺ to oxidize into Fe³⁺. A three stages mechanism: Fe₂O₃ → Fe₃O₄ → FeO (wüstite) → Fe⁰, is often postulated.

Some hexaferrites' treatments in nitrogen, hydrogen and carbon monoxide atmospheres were reported [1,2]. In those papers composition, morphology and magnetic properties were related with the gas/steam relation. A. Farghali et al. [3] carried out thermal treatments between 400 °C and 600 °C in a reducing atmosphere and concluded that the oxygen desorption mechanism is controlled by the diffusion and the interfacial chemical reactions. It was reported [4] that the treatment of hexaferrite in hydrogen atmosphere and its further annealing in open air is an alternative method to improve the coercivity of the material. In all these works the formation of intermediary phases of iron and strontium oxides was reported.

In a former paper [5] we have published the results on the preparation of strontium ferrites partially substituted with Nd³⁺ and Co²⁺. Improvements on the magnetic properties were obtained [6] and an enhancement of 47% in coercivity was achieved for the composition Sr_{0.70}Co_{0.30}Nd_{0.30}Fe_{11.70}O₁₉ (4615 Oe or 58.00 A/m) with respect to the non-substituted material, SrFe₁₂O₁₉. We observed that hematite is segregated with increasing substitution of Nd³⁺ and Co²⁺. So we proposed an iron deficient formulation: Sr_{1-x}Co_xNd_xFe_{12-x}O₁₉ in order to avoid secondary phases. We found that the best Fe/Sr relation in order to get monophasic systems lies between 10 and 11.5 [5].

* Corresponding author.

E-mail address: bercoff@famaf.unc.edu.ar (P.G. Bercoff).

In this work a larger Fe/Sr relation was intentionally chosen in order to study the reduction of the system $\text{Sr}_{0.70}\text{Co}_{0.30}\text{Nd}_{0.30}\text{Fe}_{11.70}\text{O}_{19}/\text{Fe}_2\text{O}_3$. This material, previously characterized elsewhere [6] was submitted to different thermal treatments in a hydrogen gas flow at several temperatures. The aim of this work is to structurally and magnetically characterize the particles that result from these treatments. To the best of our knowledge no similar results have been reported yet.

2. Experimental

Samples of composition $\text{Sr}_{0.70}\text{Co}_{0.30}\text{Nd}_{0.30}\text{Fe}_{11.70}\text{O}_{19}$ were prepared by the self-combustion method as it was previously reported [5]. The reactants were dissolved in HNO_3 0.1 M at room temperature and citric acid was added to the solution to complex metal cations. Finally, concentrated ammonia was added to carry the pH of the solution up to 9, approximately. The solution was partially evaporated on a heater to obtain a gel that began its self-combustion. At the end of the reaction a thin powdered mixture of precursors was obtained. This material was milled and then heated one hour at 400 °C to eliminate volatile substances. Finally, the ferrite powders were annealed in air atmosphere at 1100 °C for an hour in a program-controlled furnace. A hard magnetic material was obtained. This substance was named N.

For the reduction experiments, different samples of 50 mg were dried and milled. These samples were put in crucibles into a horizontal tubular furnace, with controlled atmosphere. During the treatments a stream of hydrogen diluted in argon (H_2 5% v/v) was flowing over the ferrite samples, at different temperatures and for different times. In all cases a N_2 flow was used before the soaking temperature was reached and after the treatment was finished, until room temperature was reached. In this way, the samples would be reduced by the H_2 flow during the desired temperature plateau of each treatment. Gas flows of about 0.6 l/minute were used. The names of the different treated samples are shown in Table 1.

All the samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and vibrating sample magnetometry (VSM). XRD determinations were made with a Philips PW3120 diffractometer using $\text{Cu K}\alpha$ radiation in the range 25–60° in 0.02° steps. Sample morphology was analyzed by SEM in a DSM 982 Gemini Zeiss microscope. A LakeShore 7300 VSM magnetometer was used to measure magnetization curves as function of

applied magnetic field (M vs H) at room temperature, up to a maximum value of 15 kOe (190 A/m).

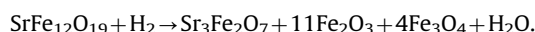
3. Results and discussion

The diffractograms of the studied samples are shown in Fig. 1. The pattern corresponding to sample N (not reduced) is shown at the top. The main phase in this sample is strontium hexaferrite and about 20% of segregated hematite can also be noticed.

This presence of Fe^{3+} oxide has been already reported in many papers on the preparation of similar ferrite samples [7–10].

The main phases that appear in the set of studied samples after the reduction process (in order of decreasing abundance) are shown in Table 1. Both Table 1 and Fig. 1 indicate that the reduction process is very sensitive to the experimental conditions of temperature and time, since the different phases relative abundances were modified (different relative intensities of the diffraction peaks). Quantitative phases determination was difficult to accomplish because of the overlapping of magnetite peaks with hexaferrite or hematite peaks.

These results indicate that the reduction process starts in the hexagonal ferrite phase, modifying it into different Sr oxides of varied stoichiometry. Hematite seems to be very stable and its abundance is increased, whereas hexaferrite diminishes, as it is shown by the following proposed reaction:



In sample N400-30, magnetite starts to appear without conclusive evidence of degradation of the hexagonal phase. This can be shown by the relative increase of the intensities ratio of hexaferrite 200/201 reflections, since the (311) family planes signal from magnetite is at the same angular position than the (201) family planes signal from hexaferrite.

In sample N500-30 a dramatic decrease in the intensity of the strongest hematite peak is observed ($2\theta = 33.12^\circ$). The increased intensity on the 200/201 reflections can be due to a greater amount of magnetite, probably yielded by the hematite already present in the material.

Table 1

Sample denomination, temperatures and times of reduction under hydrogen flow, phases in each sample (in order of decreasing abundance), maximum magnetization at 15 kOe M_{max} and coercivity H_c .

Sample	T (°C)	Time (min)	Phases	M_{max} (emu/g)	H_c (Oe)
N	–	–	$\text{SrFe}_{12}\text{O}_{19}$ Fe_2O_3	61.9	4750
N400-30	400	30	$\text{SrFe}_{12}\text{O}_{19}$ Fe_2O_3 Fe_3O_4	20.2	2590
N450-30	450	30	$\text{Sr}_3\text{Fe}_2\text{O}_7$ $\text{SrFe}_{12}\text{O}_{19}$ Fe_2O_3 Fe_3O_4 $\text{Sr}_3\text{Fe}_2\text{O}_7$	50.5	4280
N500-30	500	30	$\text{SrFe}_{12}\text{O}_{19}$ Fe_3O_4 Fe_2O_3 $\text{Sr}_3\text{Fe}_2\text{O}_7$	64.1	3490
N500-120	500	120	Fe_2O_3 Fe_3O_4 $\text{Sr}_3\text{Fe}_2\text{O}_7$	39.3	465

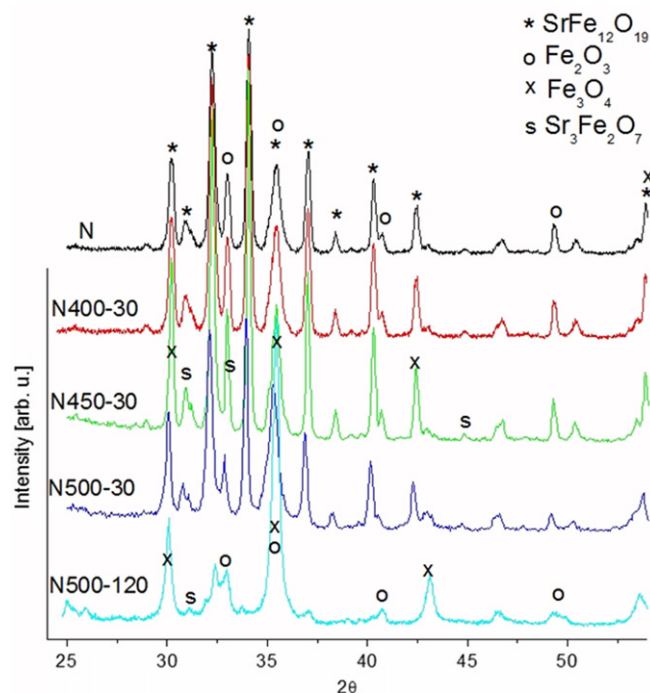


Fig. 1. Diffractograms of the studied set of samples.

The hexagonal phase is almost completely degraded in the treatment of 120 min, so an over-reduction of the sample is produced in this case. These results are quite different from those reported by A. Farghali et al. [3] where wüstite (FeO) and even metallic iron were found in samples treated at 500 °C.

The morphology of sample N is shown in Fig. 2a, where hexagonal platelet-like particles with a rather homogeneous size distribution are observed with mean diameter of 300 nm and thickness of 80 nm. During the reducing treatment this structure degrades and changes until finally (in sample N500-120), cubic crystals of 200 nm are obtained (Fig. 2b).

The M vs H curves measured at room temperature are shown in Fig. 3. Sample N has a hysteresis loop, which is typical of a hard magnetic material with a high coercivity of 4750 Oe (59.75 A/m) and a magnetization of 62.2 emu/g at 15 kOe.

As temperature and time of the reduction process increase, coercivity and magnetization tend to decrease. The values of M_{max} and H_c for all the samples are shown in Table 1.

The M vs H curves of samples N400-30, N450-30 and N500-30 are consistent with a mixture of soft and hard magnetic phases. These results agree with XRD results, where magnetite and hexaferrite are noticed. The hysteresis loop of sample N500-120 clearly shows the disappearance of the hard magnetic phase, which is also in agreement with XRD results, since this sample contains mostly magnetite and hematite.

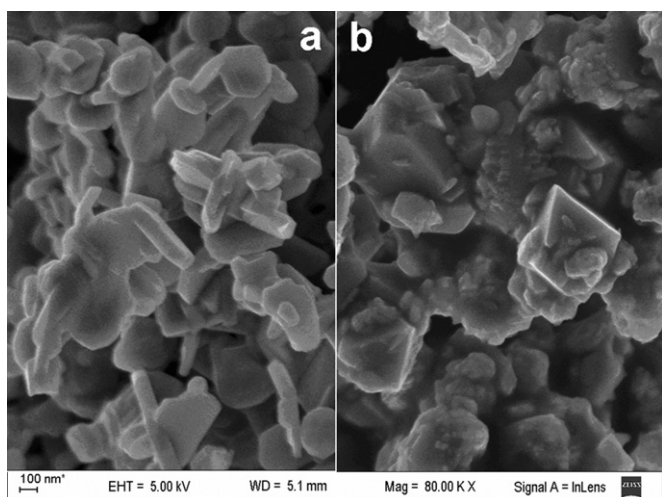


Fig. 2. SEM micrographs of samples N (a) and N500-120 (b).

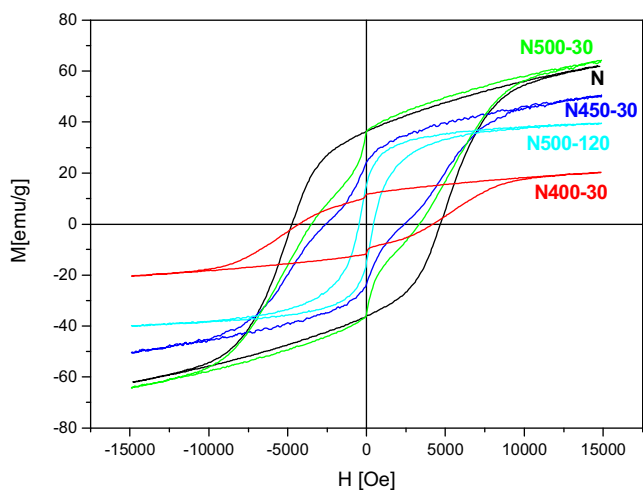


Fig. 3. Hysteresis loops of the studied samples.

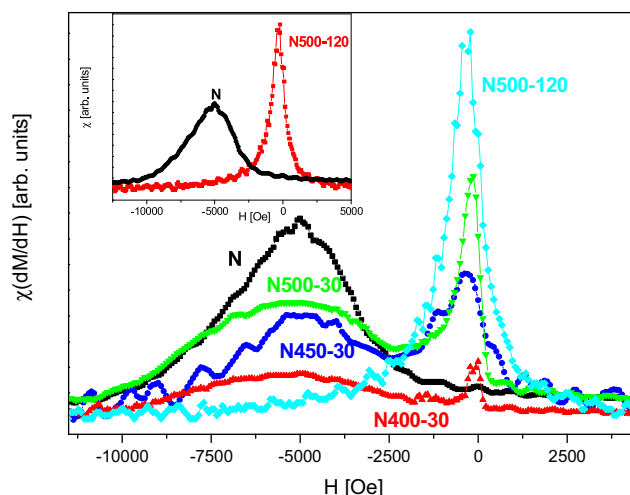


Fig. 4. Susceptibilities of the samples calculated as dM/dH . Inset: curves for the samples with only one magnetic phase.

Magnetic susceptibility is often computed as the field derivative of the superior branch of the hysteresis loop. This magnitude is related to the inversion field distributions and is particularly interesting in multi-phase samples since it can provide useful information. Each peak in χ can be related to a different magnetic phase and its maximum, denoted χ_{Hc} , is a good measure of the hardness of the material.

At room temperature, Fe_2O_3 is a weak ferromagnetic phase ($M_S \sim 0.4\text{--}0.8$ emu/g) with low coercivity in absence of defects [11], which is the case for the samples in this work (prepared by the self-combustion method and further calcination). Therefore, the contribution of hematite to the susceptibility of any of the samples in this work can be disregarded.

Fig. 4 shows the calculated susceptibilities of all the samples. The inset in Fig. 4 shows the susceptibilities of the samples with only one contribution: sample N, which contains only hexaferrite and hematite, and sample N500-120 with magnetite, hematite and small amounts of mixed Sr oxide.

The peak observed for sample N (centered in 5200 Oe) is attributed to Sr hexaferrite and the one in sample N500-120 (at 300 Oe) is assigned to magnetite. The rest of the samples display a combination of both peaks, indicating the presence of both phases. The value of χ_{Hc} that corresponds to hexaferrite remains approximately the same (5200 Oe) indicating that in all the samples the size distribution and interparticle interactions of this phase are not essentially modified. The same can be said for the soft phase (magnetite) with $\chi_{Hc} = 300$ Oe. These values of inversion fields are consistent with the coercivities of the corresponding phases.

As the temperature of the reduction treatment increases, more magnetite is formed and probably the hexaferrite is more stable. This is supported by the magnitudes of both peaks in the susceptibility, which were increased from 400 to 500 °C (Fig. 4).

The best combination of magnetization and coercivity for a hexaferrite/magnetite composite is obtained for sample N500-30. However, even when the resulting material maintains a rather high coercivity, its magnetization is only slightly improved with respect to the sample without reduction treatment. This is probably because there is still some hematite left in the sample.

4. Conclusion

In conclusion, particles of $Sr_{0.70}Co_{0.30}Nd_{0.30}Fe_{11.70}O_{19}/Fe_2O_3$ were reduced in hydrogen flow under different experimental conditions. New phases were identified at the end of each

treatment. The aim of reducing Fe_2O_3 to Fe_3O_4 to form a hard/soft magnetic composite was accomplished at different degrees according to the thermal treatment. The best results were obtained for sample N500-30, after reducing for 30 minutes at 500 °C. Lower temperatures give less magnetite and longer treatment times degrade the hexaferrite.

Further studies are being conducted on this sample in order to clarify the different phases morphological distribution.

Acknowledgments

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