



Influence of the iron content on the formation process of substituted Co–Nd strontium hexaferrite prepared by the citrate precursor method

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ABSTRACT

Strontium hexaferrite samples of different composition were prepared by the self-combustion method and heat-treated in air at 1100 °C for 2 h: $\text{SrFe}_{12}\text{O}_{19}$ (S0), $\text{Sr}_{0.7}\text{Nd}_{0.3}\text{Fe}_{11.7}\text{Co}_{0.3}\text{O}_{19}$ (SS), $\text{Sr}_{0.7}\text{Nd}_{0.3}\text{Fe}_{10.7}\text{Co}_{0.3}\text{O}_{19}$ (SM) and $\text{Sr}_{0.7}\text{Nd}_{0.3}\text{Fe}_{8.4}\text{Co}_{0.3}\text{O}_{19}$ (SL). The phase identification of the powders was performed using XRD. Only sample SL (with the lowest iron concentration) shows well-defined peaks of the hexaferrite phase with no secondary phases. Nd–Co substitution modifies saturation magnetization (M_s) and coercivity (H_c) but only samples with low Fe^{3+} content (SL and SM) show the best magnetic properties, indicating that the best results for applications of this ferrite will be obtained with an iron deficiency in the stoichiometric formulation.

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1. Introduction

Ever since their discovery by Philips between 1952 [1] and 1956 [2], M-type ferrites have increasingly become of great interest for applications such as permanent magnets, plastroferrites, injection-moulded pieces, microwave devices and magnetic recording media. At present, tremendous efforts have been made in improving their magnetic capabilities by using different synthesis methods [3,4].

It has been reported that the saturation magnetization as well as the magnetocrystalline anisotropy constant of magnetoplumbite ferrite fine particles increase by the substitution of La–Co ions [5,6]. Owing to the large ion size difference between the rare-earth element and Fe, it is very unlikely that the rare-earth element would occupy the Fe^{3+} sites. The only real possibility is the substitution of Sr by the rare-earth element. However, the solubility of rare-earth ions in Sr-hexaferrites is very low and their addition leads to the formation of secondary phases, which must be avoided in order to obtain permanent magnets with optimal properties. As hematite appears to be the main secondary phase when rare-earth ion substitution increases [7], we propose a formulation with iron deficiency.

In this paper, the structural and magnetic properties of substituted strontium hexaferrites ($\text{Sr}_{0.7}\text{Nd}_{0.3}\text{Fe}_x\text{Co}_{0.3}\text{O}_{19}$ for $x = 11.7$,

10.7 and 8.6) prepared by the self-combustion method are investigated and the influence of the Fe^{3+} content is particularly emphasized.

2. Experimental

Samples $\text{SrFe}_{12}\text{O}_{19}$ (S0: non-substituted), $\text{Sr}_{0.7}\text{Nd}_{0.3}\text{Fe}_{11.7}\text{Co}_{0.3}\text{O}_{19}$ (SS: stoichiometric), $\text{Sr}_{0.7}\text{Nd}_{0.3}\text{Fe}_{10.7}\text{Co}_{0.3}\text{O}_{19}$ (SM: medium Fe content) and $\text{Sr}_{0.7}\text{Nd}_{0.3}\text{Fe}_{8.4}\text{Co}_{0.3}\text{O}_{19}$ (SL: lowest Fe content) were prepared by the self-combustion method. The chemical precursors used for these experiments were $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, SrCO_3 , Nd_2O_3 and $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, which were weighed according to different Nd^{3+} – Sr^{2+} – Fe – Co mole ratios and completely dissolved in small amounts of a nitric acid solution. Then, the pH was adjusted to about 7 by adding ammonium hydroxide. The ratio citric:nitric acid was fixed in 2:1 for each experiment. Aqueous suspensions were stirred and heated for several hours until the sol turned into a dried gel. Then the dried gel was ignited in a corner and a combustion wave spontaneously propagated through the whole gel converting it into loose magnetic powder. The powders were calcined in air at 1100 °C for 2 h.

The structural analysis of the powders was done by X-ray diffraction (XRD) using a Philips diffractometer and $\text{CuK}\alpha$ radiation. The patterns were taken between $2\theta = 20^\circ$ and 70° with a step of 0.02° .

A vibrating sample magnetometer Lakeshore 7200 was used to measure the magnetic properties at room temperature with a maximum applied field of 15 kOe.

3. Results and discussion

The phase identification of the powders was performed using XRD. Samples S0, SS and SM reveal that the main peaks correspond to the hexagonal phase, while small amounts of hematite are present. Only sample SL shows well-defined peaks of the hexaferrite phase and no extra peaks related to secondary phases (Fig. 1).

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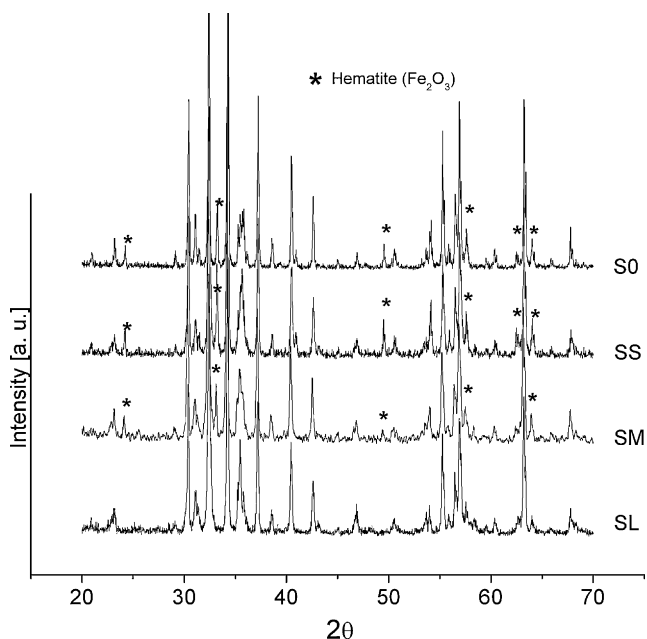


Fig. 1. Powder XRD patterns for samples S0, SS, SM and SL heat-treated at 1100 °C. All the peaks correspond to phase M of the hexaferrite, except those marked with *, which correspond to hematite (Fe_2O_3).

Using the Scherrer formula, particle sizes of about 40–50 nm were calculated for all the samples.

From the hysteresis loops of the studied samples (Fig. 2) we find that Nd–Co substitution increases the coercivity H_c with respect to S0 (the non-substituted sample) and sample SL with the lowest iron content shows the highest magnetization, reaching a maximum value $M_{\text{max}} = 72 \text{ emu/g}$ at 15 kOe. Extrapolating M vs. $1/H$ to $1/H = 0$ we find that the saturation magnetization is $M_s = 91 \text{ emu/g}$. This is a high value of saturation magnetization for this phase, as compared to other authors' results who find $M_s = 45 \text{ emu/g}$ [8]; 65 emu/g [9] and 73 emu/g [10] for Sr ferrite with La–Co substitution. The values of magnetization for samples S0, SS and SM and are not conclusive since these samples are not single-phase but contain hematite, which inhibits to determine the magnetization of the ferrite itself. However, it is possible to estimate the hematite content from XRD patterns. Using the program Philips PW-1876, relative intensities of the different phases can be compared and values as high as 28% of Fe_2O_3 in sample SS and 15% in SM were estimated. The coerciv-

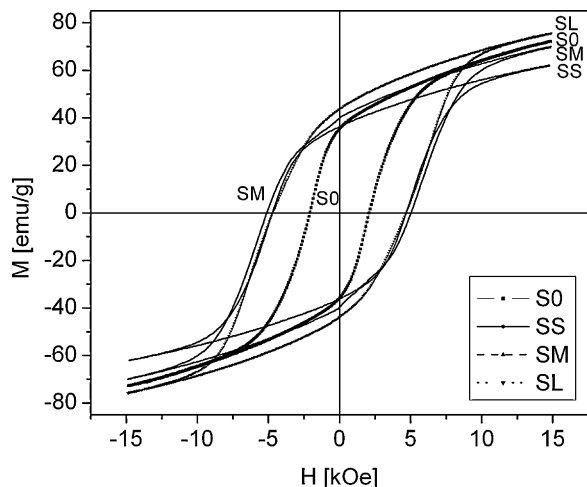


Fig. 2. Hysteresis curves for samples S0, SL, SM and SS.

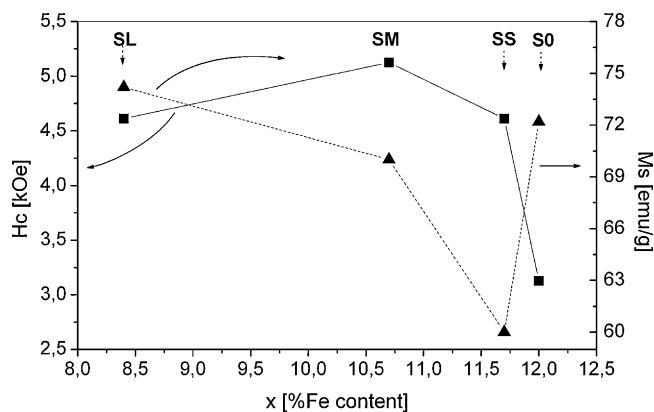


Fig. 3. H_c (left axis) and M_s (right axis) for samples S0, SL, SM and SS as a function of the iron content in each sample.

ities H_c for SS and SL are almost the same (4615 Oe and 4670 Oe, respectively) and considerably higher than the value of 3130 Oe obtained for S0. H_c for SM rises up to 5120 Oe, the highest value of the series. Fig. 3 shows H_c and M_s for all the studied samples, as a function of x , the Fe content in the formulation. From this figure it is evident that the most unfavorable combination of coercivity and maximum magnetization is obtained for the stoichiometric composition, whereas the two samples with lower Fe content (SM and SL) have much higher coercivities and reasonable values of saturation magnetization.

If we calculate the susceptibility χ as the derivative of M with respect to H of the upper branch of the hysteresis loop, we find that there is a single contribution to magnetization in the stoichiometric sample SS but there are two contributions in samples SM and SL. Fig. 4a–c shows χ vs. H and the fitting of the experimental data for the mentioned samples. The maximum dM/dH (denoted χH_c) of SS is $\chi H_c = 5630 \text{ Oe}$; the two maxima of SM are $\chi H_{c1} = 5300 \text{ Oe}$ and $\chi H_{c2} = 7120 \text{ Oe}$ and for SL are $\chi H_{c1} = 4290 \text{ Oe}$ and $\chi H_{c2} = 6685 \text{ Oe}$. These are very high coercivities for Sr ferrite, as compared to values of 3400 Oe with La, Gd and Er substitution [8], 4400 Oe [9,11] and 5000 Oe [10] with La–Co substitution.

Since from XRD data we find a single crystallographic phase in sample SL (see Fig. 1), we assign the two magnetic contributions observed in χ to an inhomogeneous cationic distribution which gives rise to two magnetic phases: a more ordered one with a coercivity of 4290 Oe and another with defects and/or vacancies which originate higher anisotropy regions and therefore raise the coercivity to the observed $\chi H_{c2} = 6685 \text{ Oe}$. Because of the interaction between these magnetic phases, H_c results in 4670 Oe for this sample. A similar analysis could be made for SM, even though this sample is not monophasic, as the amount of hematite is only 15%. The presence of this phase could be the reason why sample SM has a higher coercivity (5120 Oe).

The idea of having a harder magnetic phase because of an inhomogeneous cationic distribution has been confirmed by sintering sample SL at 1100 °C for 12 h. After this heat treatment the susceptibility can be fitted with a single peak centered in $\chi H_c = 3950 \text{ Oe}$ (Fig. 4d), probably because longer times at a high temperature allow cation diffusion to generate a homogeneous phase. The diffusion may have also been favored not only by longer times of heat treatment, but also because the sintering was done to a sample of compacted powder while calcination was done to loose powder.

We observe that an iron deficiency in the ferrite formulation favors an important enhancement in coercivity when the heat treatment is not too long. In a work by other authors [12], where Ba hexaferrite with La–Co substitution is studied, a stoichiomet-

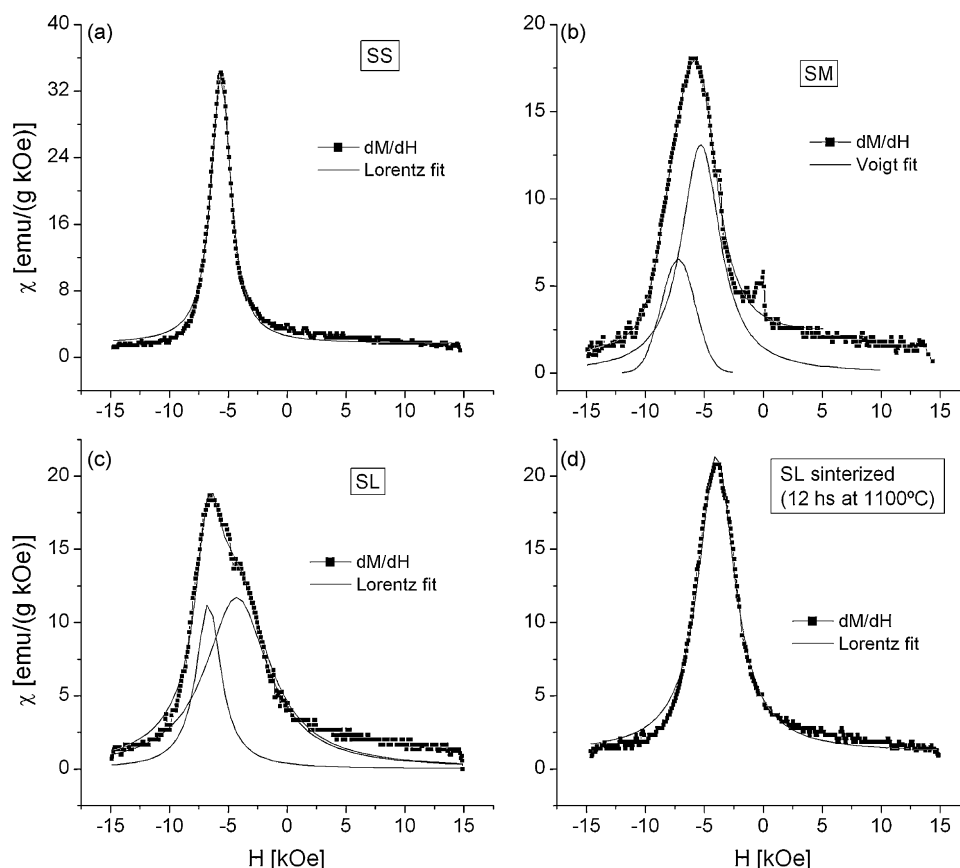


Fig. 4. Susceptibility χ for samples SS (a), SM (b) and SL (c) heat-treated at 1100 °C for 2 h, and for sample SL after sintering for 12 h at 1100 °C (d). Experimental data and fittings.

ric sample with La–Co substitution is compared to one with La excess (which implies an iron deficiency). They observe a very high coercivity of 6700 Oe for the iron-deficient sample and explain this considering that La excess both raises the anisotropy field and decouples the particles. They also find that hematite is not formed in samples with La excess. In our case we could assume that the responsible for the high χH_c is Nd and an inhomogeneous cationic distribution in the formation process that originates regions of higher anisotropy.

A detailed Mössbauer investigation on these samples has recently been published elsewhere [13]. In this work, Mössbauer analysis shows that iron occupancy is related to magnetization values and that the hyperfine parameters reflect the changes that take place in the hexaferrite structure upon Fe defect and substitution of Fe and Sr by Co and Nd.

4. Conclusions

We have successfully synthesized $\text{SrFe}_{12}\text{O}_{19}$ and $\text{Sr}_{0.7}\text{Nd}_{0.3}\text{Fe}_x\text{Co}_{0.3}\text{O}_{19}$ ($x=11.7$, 10.7 and 8.4) by the citrate precursor method, with excellent magnetic properties.

The samples with lower Fe^{3+} content show the highest saturation magnetization and/or coercivity, indicating that the best results for applications of this ferrite will be obtained with an iron deficiency in the stoichiometric formulation.

Nd substitution enhances the ferrite anisotropy and coercivity with respect to the unsubstituted sample, but the magnetic properties of Nd–Co strontium ferrite are comparable to the ones with La–Co substitution. Heat treatments should not be so long as to

prevent diffusion from homogenizing the cation distribution which results in a less coercive magnetic phase.

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