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Magnetic properties of co-precipitated hexaferrite powders with Sm-Co substitutions optimized with the molten flux method

C. Serletis[a], G. Litsardakis[b], E. Pavlidou[a], K.G. Efthimiadis[a,*]

[a] Department of Physics, Aristotle University, Thessaloniki 54124, Greece
[b] Department of Electrical & Computer Engineering, Aristotle University, Thessaloniki 54124, Greece

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ABSTRACT

In this work, using the chemical coprecipitation method, $Sr_{1-x}Sm_xFe_{12-x}Co_xO_{19}$ (x = 0, 0.1, 0.2) hexaferrite powders were prepared. Major magnetization loops were recorded at room temperature in order to determine the correct calcination temperature for optimum hard magnetic properties. It is found that a small degree of substitution increases substantially the coercive field. Also, the use of the molten flux calcination method increases the remanent magnetization. SEM/EDXS and XRD measurements were performed at the calcined powders: the results show that a single hexaferrite phase is formed and that the substituted powders consist of an assembly of grains with a mean diameter of 40 nm. Measurements of minor magnetization loops and of the temperature and time dependence of the magnetization confirm that the powders consist of a non-oriented single domain magnetic particles assembly. The results indicate that Sm could be a viable replacement for La in the manufacturing of hexaferrites with a high-energy product.

1. Introduction

Sr-hexaferrites ($SrFe_{12}O_{19}$) are magnetic materials widely used since their development in the early ‘50s. While not as powerful as the newest NdFeB or $SmCo_5$ magnets, they still have a very large share of today's market, due to their low price and easy methods of production.

Researchers attempted to improve the magnetic properties of hexaferrites by replacing Sr, Fe or both, with the main goal being to increase the magnetocrystalline anisotropy, leading to a higher coercive field. The biggest improvement was achieved when Sr was replaced with a rare earth element, with La and Gd showing the most promising results [1–3]. Still, the higher cost associated with the rare-earth elements has prevented their extensive use in hexaferrites.

Substitution with other rare earth elements was attempted, but most of the substituted materials exhibited a reduction in saturation magnetization, coercive field, or both. Also, with most rare earths, only a small degree of substitution (up to 30%) was feasible, and larger percentages led to the appearance of secondary oxide phases [4–7].

Sm-substituted hexaferrites were studied in some degree, with the results showing that pure hexaferrite phase is achieved with a substitution of 25% or less [6]. In this hexaferrite phase, reports indicate that while the coercive field increases slightly, there is a significant reduction of the saturation magnetization, attributed to the valence switch of Fe^{+3} to Fe^{+2}, in order to compensate for the higher valence of Sm^{+3} [7–11].

Han et al. [12] substituted Fe^{+3} with Co^{+2}, producing $Ba_{1-x}Sm_xFe_{12-x}Co_xO_{19}$ in order to counteract the valence switch of Fe^{+3},with results showing that for $x > 0.2$ oxide phases such as $SmFeO_3$ and $CoFe_2O_4$ appear, while both the saturation magnetization and the coercive field decrease for $x > 0$.

In this work, we synthesized $Sr_{1-x}Sm_xFe_{12-x}Co_xO_{19}$ (x = 0, 0.1, 0.2) with the chemical co-precipitation and molten flux methods. Structural and magnetic characterization was performed in order to investigate the effect that the substitutions have on the magnetic properties of the hexaferrite and to explore the viability of samarium as an alternative substitution material in hexaferrites.

2. Methodology

2.1. Chemical preparation

An aqueous solution of $Sr(NO_3)_2{\cdot}4H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$ was mixed, with $Sm(NO_3)_3{\cdot}6H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ added in for the substitutions. The ratio $[Sr^{2+} + Sm^{3+}]/[Fe^{3+} + Co^{2+}]$ was kept equal to 1/10.5, as it is reported that the excess strontium helps in the limitation of unwanted secondary phases such as $SrFe_2O_4$ [13]. An aqueous solution of NaOH was infused keeping the ratio $[OH^-]/[NO_3^-]$

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[*] Corresponding author.
E-mail address: kge@auth.gr (K.G. Efthimiadis).

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equal or greater than 2. Finally, the solution was stirred at 700 rpm for 2 h at 85 °C and filtered. The precipitate was washed and dried for 16 h at 95 °C.

2.2. Calcination procedure

The samples were pressed into pellets with a 10 t hydraulic press. The pellets were calcined in air for 2 h at a range of temperatures (800–1200 °C) in order to study the formation of the hexaferrite phase and achieve the best hard magnetic properties.

2.3. Experimental setup

The calcined powders were subjected to SEM/EDXS analysis in a JEOL JSM 840A scanning electron microscope with an INCA x-sight detector, in order to determine the atomic composition of the samples. X-ray diffraction patterns were obtained by a Seifert XRD-3003TT diffractometer using Fe K_a radiation. The magnetic characterization up to 2 T was performed with a vibrating sample magnetometer (P.A.R. 155), in a range of temperatures from 80 K to 750 K.

2.4. Molten flux calcination method

After the ideal calcination conditions were identified, the material was sintered once again from the chemical precipitate, using the molten flux method, in order to investigate the effect of the method in the magnetic properties. Here, instead of pressing the powder into a pellet, the powder was mixed in a ball mill with analytical grade NaCl with a mass ratio of 1:2 and sintered at the same conditions in an alumina crucible. Afterwards, the powder was washed to remove any remaining NaCl and dried for 16 h at 95 °C.

3. Results and discussion

SEM/EDXS characterization showed that all the samples display the nominal composition with a margin of error < 0.5%. Fig. 1 shows the SEM images captured for two different compositions.

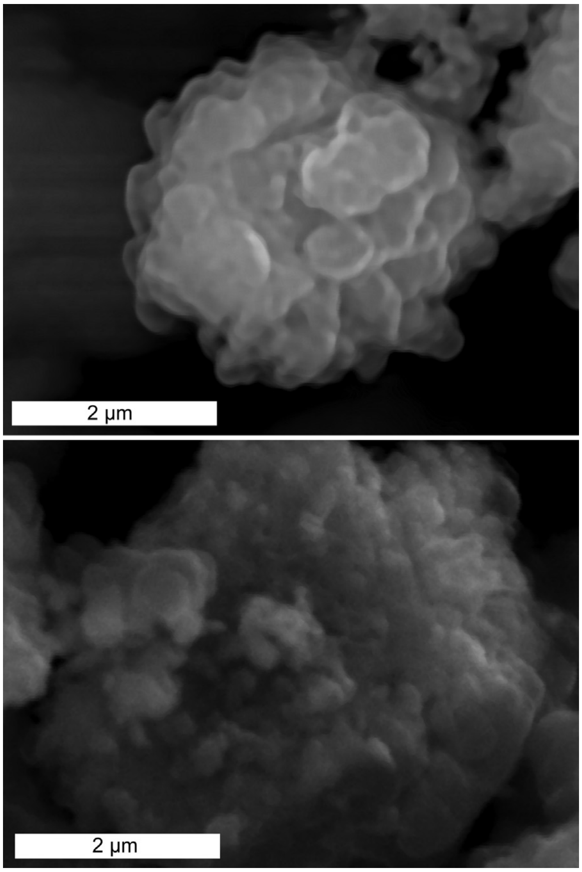

Fig. 1. SEM images of $Sr_{1-x}Sm_xFe_{12-x}Co_xO_{19}$ samples with different composition and calcination temperature (above: x = 0.1/800 °C, below: x = 0.2/900 °C).

3.1. Magnetic properties vs. calcination temperature

Fig. 2 shows the remanent magnetization and the coercive field at room temperature of the press-calcined materials vs. the calcination temperature, for each composition.

Optimum results regarding hard magnetic properties (the coercive field H_c, the remanent magnetization M_r and the energy product $(BH)_{max}$) are achieved with a different calcination temperature: while 1000 °C are required for the $SrFe_{12}O_{19}$, the presence of Sm and Co lowers the necessary calcination temperature. For a 10% substitution, the temperature becomes 800 °C, and for a 20% substitution the temperature becomes 900 °C. Figs. 3 and 4 show the major magnetization loops and the XRD patterns for the samples with the best magnetic properties.

For the unsubstituted hexaferrite (x = 0), the lower values of M_r and H_c at 800 °C and 900 °C can be attributed to the presence of secondary oxide phases ($SrFe_2O_4$), as determined by X-ray diffraction patterns, indicating that the hexaferrite phase was not fully formed at these low temperatures. At higher temperatures (> 1000 °C), despite the formation of a pure hexaferrite phase, the values of M_r and H_c decrease again due to the excessive grain growth in the material.

The sample with x = 0.1 showed the best overall magnetic properties, with a pure hexaferrite phase forming at 800 °C and having the highest M_r and H_c. At 900 °C, grain growth lowers the values of M_r and H_c, while at higher temperatures the material decomposes and displays increasing oxide content (Fe_2O_3 and $SmFeO_3$), as determined again by X-ray diffraction.

For the sample with x = 0.2, the results were mixed: at 800 °C the hexaferrite phase does not fully form, indicating that more energy is required in order for the excess Sm to replace Sr. Pure phases are obtained at 900 °C and 1000 °C. We determine the best overall magnetic properties to be found at the 900 °C, since it has a slightly better energy product $(BH)_{max}$, even though at 1000 °C the remanent magnetization is found to be much higher. At higher temperatures the material decomposes, as was the case with the previous sample.

The inconsistency in the calcination temperatures can be attributed to the effect of the substitutions: at 10% substitution it appears that the presence of Sm and Co helps in the creation of the structure. At 20% substitution, the excess Sm inhibits the formation of the crystal grid, as we approach the solubility limit of 25% where Sm oxides begin to appear as a secondary phase.

Consequently, the material chosen for further study was $Sr_{0.9}Sm_{0.1}Fe_{11.9}Co_{0.1}O_{19}$, calcined at 800 °C, due to its very high coercive field. Samples with this composition were sintered once again from the chemical precipitate, using the molten flux method, in order to investigate the effect of the method in the magnetic properties. Fig. 5 shows the major magnetization loops of both the press-calcined and flux-calcined materials. Fig. 6 shows the XRD pattern of the flux-calcined material.

The comparison of major magnetization loops (Fig. 5) for the two calcination methods show that, while the coercive field remains unchanged, there is an increase in the saturation and remanent magnetization, which improves the energy product $(BH)_{max}$.

The X-ray diffraction pattern of the flux-calcined powder shows no evidence of phases other than the hexaferrite phase (Fig. 6). All peaks are typically indexed as M-type hexaferrite (space group P63/mmc, a = 5.875 Å and c = 23.015 Å, JCPDS Card 84-0757). The result of the application of the Scherrer equation on the most intensive peaks is that the diameter of the particles is roughly 40 nm. Since the critical