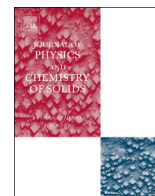




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Hard magnetic properties of nanosized Sr(Fe,Al)₁₂O₁₉ hexaferrites obtained by Pechini method

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ABSTRACT

In this work, we report the magnetic properties of isotropic M-type SrFe_{12-x}Al_xO₁₉ (x=0,0.1,5) hexaferrites synthesized by means of Pechini method. A polycrystalline distribution of fine grains was verified by Transmission Electron Microscopy for both compositions, with average sizes below 60 nm. Remarkable coercivity values within the range 500–850 kA/m were attained as a consequence of a combined effect of grain size refinement together with an enhancement of the anisotropy field afforded by the incorporation of the Al³⁺ cations into the hexagonal crystal structure.

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1. Introduction

Permanent magnets are an important class of functional materials due to their wide technological application field, including small motors, actuators, generators, medical and microwave devices, and more recently, emerging applications related to automobile industry [1,2]. Hard ferrites with magnetoplumbite structure (also known as M-type hexaferrites) occupies a significant place in the permanent magnet market due to their competitive cost per unit of stored energy, their excellent chemical stability and their high Curie temperature, usually well above 600 K [3–6]. These materials have been widely used for fabrication of decoration magnets or as anisotropic components in loudspeakers or small motors. In addition, the considerable magnetocrystalline anisotropy characteristic of the hexagonal M-type structure favors typically coercivity field values of around 400 kA/m, which falls within the low field range of nanocomposite Nd–Fe–B hard magnets with low rare earth content (i.e., below 8 at%) [7,8]. Although numerous partial Sr/Fe substitutions have been extensively reported for SrFe₁₂O₁₉ ferrites with variable effect on their magnetic performance [5,9,10], the best choice for attaining coercivity values in excess of 400 kA/m is partial Fe replacement by Al, for which coercivity values as high as 800 kA/m have been reported [10,11]. Coercivity indicates the ability of the material to resist

demagnetization reversal under the application of an external field. Other figures of merit to evaluate the magnetic performance of permanent magnets are the remanence magnetization and the saturation magnetization [1,2,7].

An important number of synthetic routes have been reported for obtaining pure and doped M-type hexaferrites with variable coercivity values, like self-combustion method, solid state reaction, sol–gel, co-precipitation and polymerizable complex method, among others [3–5,9,12]. An alternative way to obtain nanosized hexaferrites is the “Pechini method”. In this synthetic route, an alpha hydroxycarboxylic acid (like citric acid) is used to chelate with various cationic precursors by forming a polybasic acid. In the presence of a polyhydroxyl alcohol like (ethylene glycol), the chelate reacts to form organic esters and water by-products. When the mixture is heated, polyesterification occurs and leads to a homogeneous sol in which metal ions are uniformly distributed throughout the organic matrix. When the sol is further heated to remove the excess of solvents, an intermediate resin will be formed. The solid resin is then heated to elevated temperatures to remove organic residuals. The aimed stoichiometric compounds are formed during the pyrolysis. Due to the homogeneity of the ions spreading, as well as the formation of small particles with narrow size distribution, the diffusion of cations towards the formation of the product phase is feasible for reaction temperatures lower than 1000 °C [13]. In this work, we report and discuss the magnetic properties of nanosized Sr(Fe,Al)₁₂O₁₉ hexaferrites obtained by means of the Pechini method by using calcination

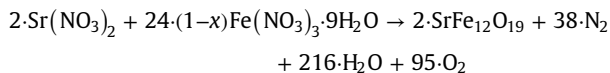
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temperatures below 1000 °C, alongside coercivity enhancement over 800 kA/m.

2. Experimental techniques

M-type hexaferrites with formula $\text{SrFe}_{12-x}\text{Al}_x\text{O}_{19}$ ($x=0.0, 1.5$) were synthesized by means of the Pechini method. The following precursors were used: $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Mallinckrodt, $\geq 99.0\%$), $\text{Sr}(\text{NO}_3)_2$ (Fluka $\geq 99.0\%$) and $\text{Al}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Aldrich $\geq 98.0\%$). The synthetic route was the following: For each nitrate, weighed according to the stoichiometry of each composition, an individual dissolution in distilled water was prepared. After two hours of stirring, all the dissolutions were mixed in a single one. The polymeric resin was formed separately by the addition of citric acid and ethyleneglycol in the molar proportion 1:14, by heating at 70 °C during 30 min. At this point, the nitrates dissolution was added to the resin and kept under continuous stirring during 3 h at 90 °C, until the water evaporated. The resultant dried polymer was grounded for the following sequence of calcination treatments in a muffle (Thermolyne 47900): 200 °C for 12 h, 400 °C for 4 h, 700 °C for 18 h and 800 °C for 24 h. These synthetic conditions are milder than those reported for equivalent $\text{SrFe}_{12-x}\text{Al}_x\text{O}_{19}$ hexaferrites in [10,11], for which annealing temperatures ≥ 950 °C were used, alongside hydrochloric acid for dissolving the glassy matrix in one case. The proposed reaction for the $\text{SrFe}_{12}\text{O}_{19}$ hexaferrite is the following:



Phase distribution and grain size features were determined by means of XRD diffraction in a Bruker AXS D8 equipment with $\text{Co-K}\alpha$ radiation and by using Transmission Electron Microscopy (TEM) in a JEOL 1200 equipment operating at 20 kV. Additionally, grain morphology was verified by Scanning Electron Microscopy in a Jeol F7600 equipment. The magnetic properties at room temperature were determined by means of Vibrating Sample Magnetometry (VSM) in a LDJ 9600 equipment with $H_{\text{max}}=1250$ kA/m, whereas the Curie temperature was established by means of Magnetic Thermogravimetric Analysis (MTGA) in a thermobalance within the temperature range 300–980 K at a heating rate of 10 K/min under an applied field of 160 kA/m.

3. Results

X-ray diffractograms for the $\text{SrFe}_{12-x}\text{Al}_x\text{O}_{19}$ hexaferrites are shown in Fig. 1. All the peaks correspond to the hexagonal M-type $\text{SrFe}_{12}\text{O}_{19}$ phase, according to the ICDD file # 01-084-1531. No extra peaks related to secondary phases are observed. The Al^{3+} substitution into the hexagonal crystal structure is expected to occur due to the accomplishment of the rule of charge conservation [6].

Rietveld analysis was performed for both compositions in order to verify the formation of a single phase, as shown in Fig. 2 for the $\text{SrFe}_{10.5}\text{Al}_{1.5}\text{O}_{19}$ hexaferrite as example. The contribution of the sample holder (made of SiO_2) was taken into account for the fitting process at low angles, giving an excellent match with experimental data, as indicated by all the R factors (R_{exp} , R_{wp} , R_p and χ^2) shown in Table 1, together with the structural parameters resulting from the fitting process (for both compositions). Additionally, the refined atomic positions and the occupation factors for all the crystallographic sites as well as the bond distance together with the bond angle, are displayed for the $\text{SrFe}_{12}\text{O}_{19}$ hexaferrite in Tables 2 and 3. For the $\text{SrFe}_{10.5}\text{Al}_{1.5}\text{O}_{19}$ sample, same data are

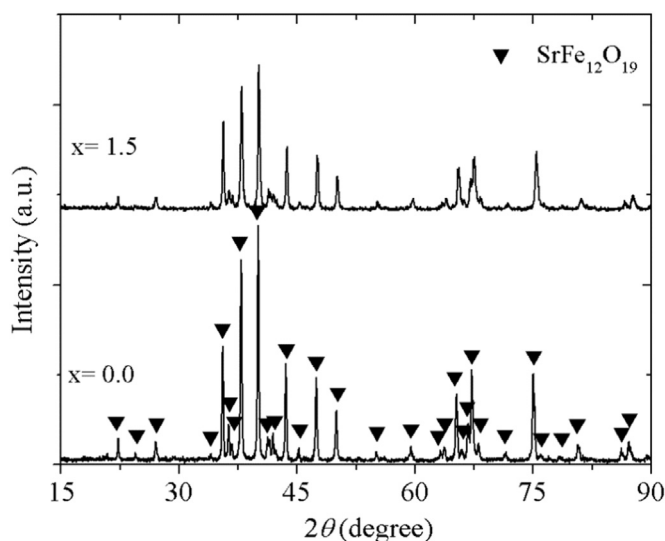


Fig. 1. X-ray diffractograms for the $\text{SrFe}_{12-x}\text{Al}_x\text{O}_{19}$ hexaferrites.

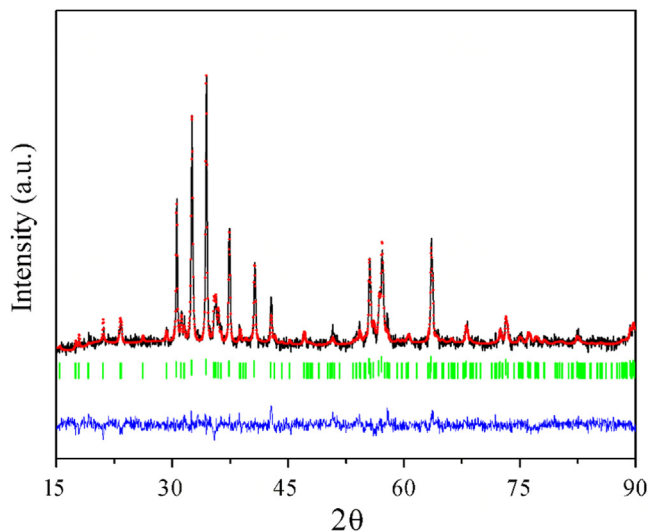


Fig. 2. Experimental (solid black line) and calculated (dots in red) X-ray diffraction profiles for the $\text{SrFe}_{10.5}\text{Al}_{1.5}\text{O}_{19}$ hexaferrite. Tick marks below the diffraction pattern represent the allowed Bragg reflections. The difference profile is located at the bottom of the figure as a blue line. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1

Structural parameters and R factors from Rietveld analysis for $\text{SrFe}_{12-x}\text{Al}_x\text{O}_{19}$ hexaferrites.

Parameter	$\text{SrFe}_{12}\text{O}_{19}$	$\text{SrFe}_{10.5}\text{Al}_{1.5}\text{O}_{19}$
Unit cell (Å)	$a=5.891, c=23.084$	$a=5.855, c=22.969$
Crystallite size (nm)	61.4	58.9
Volume (Å ³)	693.7	682.1
Density (g/cm ³)	5.08	4.95
R_{exp} (%)	1.703	1.775
R_{wp} (%)	3.604	2.270
R_p (%)	2.6	1.812
χ^2	2.117	1.279

displayed in Tables 4 and 5.

$\text{SrFe}_{12}\text{O}_{19}$ hexaferrite has a magnetoplumbite-type crystal structure, comprising alternative stacks of spinel S (Fe_6O_8) and hexagonal R ($\text{SrFe}_6\text{O}_{11}$) blocks in the form of RSR^*S^* , where $*$ denotes 180° rotation around the hexagonal c -axis. Within the unit

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