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Effect of rare earth substitution in cobalt ferrite bulk materials

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ABSTRACT

The study was focused on the influence of small amounts of rare earth (RE=La, Ce, Sm, Gd, Dy, Ho, Er, Yb) addition on the microstructure, phase content and magnetic properties of cobalt ferrite bulk materials. The X-Ray diffraction measurements confirmed the formation of the spinel structure but also the presence of secondary phases of RE oxides or orthoferrite in small percentages (up to 3%). Density measurements obtained by Archimedes method revealed a ~1 g cm^{-3} decrease for the RE doped cobalt ferrite samples compared with stoichiometric one. Both the Mössbauer and Fourier Transform Infrared Spectrocopy analysis results confirmed the formation of the spinel phase. The saturation magnetization and coercive field values of the doped samples obtained by Vibrating Sample Magnetometry were close to those of the pure cobalt ferrite. For magnetostrictive property studies the samples were analyzed using the strain gauge method. Higher maximum magnetostriction coefficients were found for the Ho, Ce, Sm and Yb doped cobalt ferrite bulk materials as related to the stoichiometric $CoFe_2O_4$ sample. Moreover, improved strain derivative was observed for these samples but at higher magnetic fields due to the low increase of the coercive field values for doped samples.

1. Introduction

Cobalt ferrite materials have attracted a great interest in fundamental and applied research due to their thermal stability, mechanical hardness, large coercive field, high magnetostriction coefficient and anisotropy constant. All these characteristics encourage their use in a wide range of applications from medicine (e.g.: MRI contrast agents [1], DNA isolation [2], magnetically activated drug delivery [3]) to electronics (e.g.: magnetostrictive and gas sensors [4], optoelectronics, microwave frequency devices [5], storage media [6]). Relating to all these possible applications, different research groups performed various studies on the influence rare earths cations on the properties of $CoFe_2O_4$ in bulk form [7], thin films [8] or nanoparticles [9,10].

Based on the large Faraday effect in the spectral ranges 700–800 and 400–500 nm, cobalt ferrite is considered as a possible alternative for magneto-optical (MO) devices which are included not only in magnetic recording [11] but also in light modulators and deflectors [12]. The use of cobalt ferrite as MO recording media is impaired by the high Curie temperature which challenges the thermal-magnetic writing. Among other effects, rare earth ions are reported to lower the Curie temperature and increase the MO response when present in ferrite structures [8,12–14]. Cheng et al. obtained an increase in polar Kerr rotation from 0.6° to 1° for the Er and Tm doped cobalt ferrite films annealed at 800 °C for 1 h, while no significant changes in MO response was observed for the Ho, Yb and Lu ion substitution. The RE substitution can also decrease the grain size, which is an important factor in low noise media [12].

Another interesting property of cobalt ferrite is the infrared emissivity which can also be improved by changing the distribution and nature of the cations in the spinel ferrite [15]. Zang et al. reported an increase in infrared emissivity up to 7% for the 8–14 μm wave bands when adding rare earth elements into cobalt-based ferrites [16,17].

All the mentioned results sustain the importance of research studies based on the influence of RE addition on the properties of cobalt ferrite. The interest in rare earth elements and their influence on the microstructure and magnetic properties of substituted ferrite is related to the occupancy of the 4f electron shell (from 0 (La) to 14 (Lu)) and magnetic moments (from 0 (La) to 10.6 μ_B (Dy)). Due to their moderate elastic constants and the large orbital component in their moments, the lanthanide metals display the largest known magnetostrictions [18]. The RE elements present large ionic radii which, when substituting cations with smaller ionic radii in other types of structures, can determine a change in cell symmetry and thus generate internal stress. As a consequence, not only the structural properties of the material are changed (e.g. increased cell parameter, decreased average crystallite and grain dimensions) but also the dielectric, magnetic and magnetostrictive

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properties of substituted materials [19,20]. While in bulk materials the presence of RE elements leads to residual phase formation and decreased magnetic response [7], in thin films and nanocrystals only the spinel lattice is observed [21–23] with an increased magnetization for the RE elements with higher magnetic moment than Fe [24].

This paper presents the structural, magnetic and magnetostrictive properties of pure and RE (La, Ce, Sm, Gd, Dy, Ho, Er and Yb) doped cobalt ferrite bulk materials obtained by solid state reaction. To the best of our knowledge these are the first magnetostriction measurements reported for a large series of rare earth substituted cobalt ferrite bulk materials.

2. Experimental details

RE doped cobalt ferrite bulk materials with chemical formula $CoFe_{1.97}RE_{0.03}O_4$ (RE=La, Ce, Sm, Gd, Dy, Ho, Er, Yb) were obtained by conventional ceramic technique. Considering our previous results on $CoFe_{1.8}RE_{0.2}O_4$ bulks where the high RE concentration determined an up to 12% residual orthoferrite phase concentration [7], in this study we used a smaller amount of RE oxide in powder synthesis. Commercially available pure oxides (Fe_2O_3, Co_3O_4 and RE_2O_3) were used as starting materials, mixed in adequate proportions, calcined in air at 950 °C for 5 h and then ball milled for 8 h. Finally the milled powders were pressed into disks at 250 MPa and sintered in air at 1250 °C for 5 h with a 100 °C/h heating rate followed by a natural cooling to room temperature [7]. The selection of these sintering conditions was based in the study of other research groups [25,26] which reported that the 1250 °C sintering temperature is enough to obtain a spinel structure with no residual phases and high magnetostriction coefficients. For comparison, a stoichiometric cobalt ferrite sample was also prepared in the same conditions as the doped ones.

For the structural characterization of the resulting calcined powders and sintered pallets, different subsequent analyzing methods were used: X-Ray diffraction (XRD Bruker D8 advanced diffractometer with a Cu-Kα radiation, λ=1.5406 Å), Mössbauer spectroscopy (WissEL-ICE Oxford Mössbauer cryomagnetic system), Fourier transform infrared spectroscopy (FT-IR – JASCO 660 Plus spectrophotometer), Scanning Electron Microscopy and Energy-Dispersive X-ray spectroscopy analysis (SEM/EDX, Vega Tescan LMH II microscope and a Bruker AXS Microanalysis GmbH detector). The magnetic behavior was investigated by Vibrating Sample Magnetometry (VSM PRINCETON/Lakeshore M3900) while the magnetostriction coefficient and its field derivative were measured using the strain gauge method with a homemade set-up described in [27]. For dielectric constants measurement an E4980A Precision LCR Meter was used to analyze the real permittivity and tangent loss values from 20 Hz to 20 MHz frequency range.

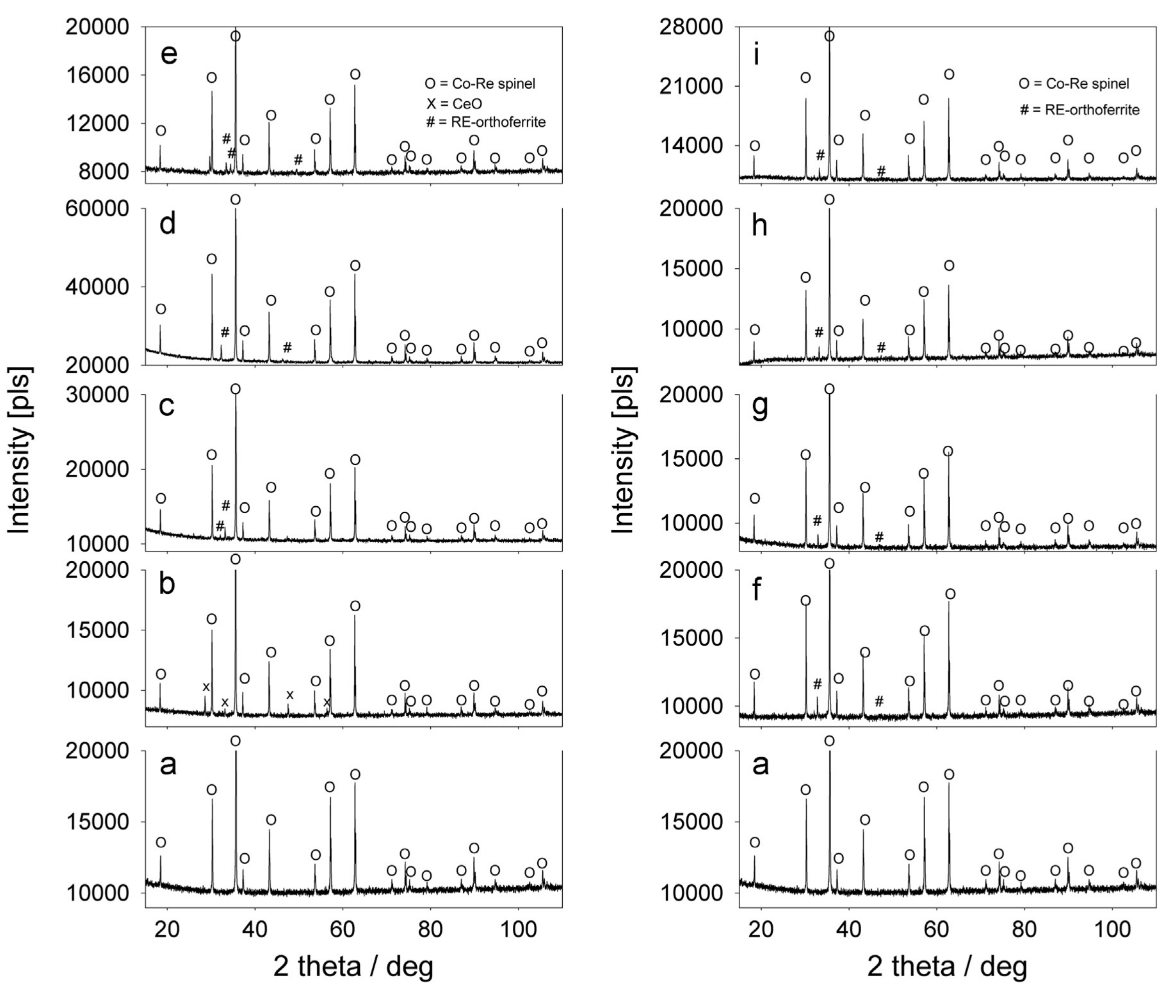

Fig. 1. XRD patterns of the sintered undoped (a) and RE doped (b–i) $CoFe_{1.97}$ $RE_{0.03}O_4$ (RE=Ce, Dy, La, Yb, Sm, Gd, Ho and Er).