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Stabilization of scandium rich spinel ferrite $CoFe_{2-x}Sc_xO_4$ ($x \leq 1$) in thin films

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ABSTRACT

Scandium rich cobalt ferrites $Co_yFe_{3-x-y}Sc_xO_4$ with $y\sim1$ never obtained in bulk could be stabilized in pulsed laser deposited thin films. Scandium contents of up to $x=1$ are reached. The cell parameter increases versus x as awaited when considering the size of scandium. It is equal to 0.8620 nm for $x=1$, significantly higher than that of $CoFe_2O_4$ (0.8396 nm). The lattice mismatch between the MgO (100) substrate and the scandium-containing spinel leads to an increased roughness. Cobalt is displaced from the octahedral site by Sc and mainly occupies the tetrahedral sites for high x values.

1. Introduction

Spinel-type oxides of general chemical formula AB_2O_4 have been known for a long time. They have given rise to many technological applications in magnetic recording, batteries, catalysis or biomedicine [1–5]. The reason for this success is the numerous possibilities that the cristallographic structure offers [6], It can be described as a close packed face centered cubic (fcc) arrangement of 32 oxygen anions O^{2-} designing 64 tetrahedral (Td) and 32 octahedral [Oh] sites [7]. One eighth of the Td sites and half of the Oh sites are occupied. Each cubic unit cell contains eight AB_2O_4 formula units. Depending upon the cation size and affinity to tetrahedral or octahedral environments, A and B distribute on the two sites according to $(A_{1-s}B_s)[A_sB_{2-s}]O_4$, s varying between $s=0$ (normal spinel) and $s=1$ (inverse spinel). A great variety of spinels having striking properties in magnetism, conductivity, thermal stability has been elaborated [8–10]. The magnetic behavior of spinel ferrites spreads from paramagnetism at room temperature (zinc ferrite), soft (manganese ferrite) or hard (cobalt ferrite) ferrimagnetism and allows everyday life uses of these materials for magnetic recording, motors, electromagnetic wave absorbers, …. The last decade has seen an impressive renewal of interest for these spinel ferrites in general, and for $CoFe_2O_4$ in particular. This increasing interest originates from the possibility to control the anisotropy of this material in thin films through the choice of the substrate or the association with other functional oxides such as ferroelectric oxides [11–16].

Generally, the metallic sites are occupied by cations belonging to the first four lines of the periodic table. Many attempts have been done to substitute rare earth for iron in spinel ferrites. This could allow increasing the magnetocrystalline anisotropy resulting from a competition between the strong spin-orbital coupling of the 4f element and the crystal field. This phenomenon is characterized by a modification of the anisotropy constants and is well known in the garnet type RFe_5O_{12} compounds as well as in the perovskite $RFeO_3$-type materials ([17] ,and Ref. therein). However, the quantity of RE involved is always low due to the size of the RE cations with respect to transition metals. Zhou et al. succeeded to stabilize nanocrystalline $CoFe_{2-x}Sc_xO_4$ films prepared by sol–gel process for x up to 0.4 18,. Ben Tahar et al. and Kahn et al. have synthesized $CoFe_{1.9}RE_{0.1}O_4$ and $CoFe_{1.88}RE_{0.12}O_4$ (RE=La–Ho) nanoparticles by forced hydrolysis in polyol and micellar routes, respectively [19,20]. Raman et al. have tried to substitute Gd for Fe but $GdFeO_3$ peaks are visible for Gd to Fe ratios higher than 0.05 [21], Recent preparations of $CoRE_xFe_{2-x}O_4$ (RE=Nd, Sm and Gd) by the chemical co-precipitation method or by pulsed laser deposition (PLD) have been performed for values of x up to 0.2 [22–25].

We present here the elaboration of $CoFe_{2-x}Sc_xO_4$ thin films on MgO (100) substrates by PLD. Scandium has chemical properties

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close to the RE ones, an analogous electronic configuration and a size larger than that of the transition elements. Therefore, it can be considered as 'prototype', sharing all the properties of the lanthanides that are not dependent upon the 4f electrons. In a previous work, $CoFe_{2-x}Sc_xO_4$ bulk spinel phases were stabilized for $x \leq 0.56$ [26]. For x higher than 0.2, Co^{3+} and cationic vacancies were evidenced, Sc_2O_3 was always present as an additional phase and the variation of the lattice parameter versus x was not linear. We show that thin films are favorable for the stabilization of pure spinel $CoFe_{2-x}Sc_xO_4$ for values of x up to 1.

2. Materials and methods

2.1. Preparation of $CoFe_2O_4$, CoO and Sc_2O_3 targets

The targets were prepared by sintering the oxide powders at high temperature. $CoFe_2O_4$ powder was obtained by adding dropwise a stoechiometric mixture of $FeCl_3,6H_2O$ and $CoCl_2,6H_2O$ (99% Alfa Aeasar) into a 14 M boiling KOH solution. The resulting precipitate was left to boil for 30 min in order to favor the Ostwald ripening. It was then filtered, washed with hot water until no more Cl^- was detected in the filtration water, and annealed at 100 °C in air for 24 h. The resulting powder was manually ground. An organic binder (polyvinylalcohol) was systematically added at around 3 wt% to improve the mechanical behavior of the samples. The powders were finally compacted into pellets and sintered in a platinum crucible at 1200 °C for 12 h under air. In a similar way, Co_3O_4 (99% Alfa Aeasar) and Sc_2O_3 (99.9% Alfa Aeasar) commercial powders were sintered at 950 °C in H_2/N_2 (10/90) during 20 h and at 1200 °C during 20 h in air respectively to elaborate CoO and Sc_2O_3 targets.

2.2. Elaboration of thin films

Films have been elaborated by Pulsed Laser Deposition (PLD) using a KrF excimer laser $\lambda = 248$ nm with a 10 Hz repetition rate and the three targets ($CoFe_2O_4$, CoO and Sc_2O_3). The composition of the $CoFe_{2-x}Sc_xO_4$ films was varied by adjusting the number of laser shots on Sc_2O_3, $CoFe_2O_4$ and CoO targets. The films were deposited on MgO (100) substrates. MgO has a rock salt type structure whose lattice parameter $a = 0.4210$ nm is close to half the cobalt ferrite parameter, in favor of an epitaxial growth. The energy density of the laser on the target was tuned to 1 J/cm^2 and the distance between the target and the substrate was fixed at 5 cm. Layers of about 60 nm thickness were deposited under 0.1 mbar O_2 at 450 °C. After the deposition, the samples were cooled down to room temperature under the processing gas

The crystallographic structure was characterized by X-ray diffraction (XRD). $\theta - 2\theta$ scans were performed using a D-5000 diffractometer equipped with copper radiation ($K\alpha = 0.154056$ nm). The surface of the thin films was observed by scanning electron microscopy (JEOL 6700F) coupled with energy dispersion X-ray analysis (SEM-EDX) and atomic force microscopy (AFM) (Digital Instruments Dimension 3100 AFM). AFM was performed at a scan rate of 0.5 Hz with a 125 μm long tapping mode Nanosensors Si cantilever having a force constant of 42 N/m and a resonance frequency of 300 kHz. The chemical composition of the films was determined from SEM-EDX. The values given in Table 1 are an average over at least five measurements performed at different locations on the sample, with a standard deviation inferior to 1 wt%. The magnetic properties were studied using a superconducting quantum interference device magnetometer (SQUID MPMS XL, Quantum Design).

Table 1
Scandium content of the $CoFe_{2-x}Sc_xO_4$ spinel thin layers deduced from energy dispersive X-ray (EDX) analysis, cell parameters calculated from the (004) and (008) diffraction lines and roughness from AFM.

Co	0.98(2)	1.08(2)	1.10(2)	1.09(3)	1.12(2)	1.15(2)
Fe	2.01(2)	1.62(2)	1.45(2)	1.26(2)	1.03(3)	0.85(2)
Sc (=x)	0.00(2)	0.30(2)	0.45(2)	0.65(2)	0.85(2)	1.00(2)
Cell parameter a (nm)	0.8382	0.8451	0.8486	0.8550	0.8590	0.8620
Roughness (rms in nm)	1.2(3)	5.7(2)	5.6(2)	3.6(4)	4.2(2)	3.0(3)

3. Results

The patterns recorded on scandium doped cobalt ferrite thin films exhibit intense peaks corresponding to the (200) and (400) MgO diffraction lines, that have been cut in Fig. 1a and b. The comparison between the $CoFe_2O_4$ patterns recorded on thin film and on powder sample shows that an epitaxial growth of $CoFe_2O_4$ is observed on MgO. Close to MgO peaks but weaker, the (400) and (800) Bragg peaks of the spinel phase are visible (Fig. 1a). These peaks are shifted towards the low diffraction angles for $CoFeScO_4$ thin film. Moreover reciprocal space mappings have been performed around the (840) and (420) peaks of the CFO and MgO, respectively. The map obtained for the $x = 0.65$ film is given in Fig. 2 as an example. It clearly evidences that the CFO film is perfectly strained on the substrate. The out of plane lattice parameter is increased from 0.8382 nm up to 0.8620 nm and can be accounted for the higher value of the Sc^{3+} ionic radius with respect to the Fe^{3+} one [27]. No peak corresponding to other reflections or phases is evidenced for x between 0 and 1 (Fig. 1b). For $x = 1.2$, the (004) and (008) diffraction lines are enlarged and an additional peak corresponding to α-Fe_2O_3 appears. Therefore, $x = 1$ can be considered as a limit for the elaboration of pure Sc-containing cobalt ferrite. The cell parameters measured on thin films are displayed in Table 1. They increase quasi-linearly versus the scandium content (Fig. 3). The variation of the spinel lattice parameter can be expressed by:

$$a = \frac{40}{11\sqrt{3}}\alpha + \sqrt{\frac{64}{11}\beta^2 - \frac{512}{363}\alpha^2} \quad (1)$$

where α and β are the average cation-oxygen distances in tetrahedral and octahedral sites, respectively [28], These distances are given in Table 2 for Co^{2+} and Fe^{3+} in octahedral and tetrahedral sites and for Sc^{3+} in octahedral site. Generally, cobalt ferrite is assumed to be an inverse spinel with all cobalt atoms in the octahedral site. However, the inversion degree can be varied according to the thermal history of the sample. In order to take that into account, the inversion degree s is introduced. The α and β parameters of Eq. (1) can be thus expressed by:

$$\alpha = (1 - s)\,\alpha_{Fe} + s\,\alpha_{Co} \quad (2)$$

and

$$\beta = 1/2\left[(1 - s)\beta_{Co} + (1 + s - x)\beta_{Fe} + x\beta_{Sc}\right] \quad (3)$$

where s represents the inversion degree and x the scandium content. The theoretical variation of lattice parameters according to Eqs. (1), (2) and (3) for cationic values reported in Table 1 has been drawn versus the scandium content (x) for the three inversion degrees, $s = 0$, 0.5 and 1 (Fig. 3). In the three cases, the variation is almost linear. The experimental cell parameters can be fitted with the $s = 0$ straight line (inverse spinel) for $x \leq 0.45$, whereas the $s = 0.5$ straight line is the closest to the experimental values for $x \geq 0.65$. For low x values, the spinel is therefore an inverse spinel with all the cobalt ions in the octahedral sites. The increasing number of scandium in the ferrite structure shifts the