



## Preparation of iron cobaltite thin films by RF magnetron sputtering



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### ABSTRACT

Iron cobaltite thin films with spinel structure have been elaborated by radio-frequency (RF) magnetron sputtering from a  $\text{Co}_{1.75}\text{Fe}_{1.25}\text{O}_4$  target. Influence of argon pressure on structure, microstructure and physical properties of films has been examined. Iron–cobalt oxide thin films essentially consist of one spinel phase when deposited at low pressure (0.5 and 1.0 Pa). At high pressure (2.0 Pa), the global stoichiometry of the film is changed which results in the precipitation of a mixed monoxide of cobalt and iron beside the spinel phase. This in-situ reduction due to an oxygen loss occurring mainly at high deposition pressure has been revealed by X-ray diffraction and Raman spectroscopy. Microstructural evolution of thin film with argon pressure has been shown by microscopic observations (AFM and SEM). The evolution of magnetic and electrical properties, versus argon pressure, has been also studied by SQUID and 4 point probe measurements.

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### 1. Introduction

Transition–metal oxides with spinel structure have been intensively investigated over decades for potential technological applications due to their variety of interesting physical and chemical properties. Spinel oxides are described by the general formula  $\text{A}[\text{B}_2]\text{O}_4$  with A and B representing tetrahedral (Td) and octahedral (Oh) sites, respectively. The divalent cations occupy Td sites and the trivalent cations occupy Oh sites in normal spinels [1]. But for disordered spinels or inverse spinels, tetrahedral sites can be occupied partially or totally by the trivalent cations [2–5]. Such structure tends to exhibit varying physical properties depending on nature of transition-metal cations and their distribution between two crystalline sites [6,7].

Iron cobaltites exhibit excellent chemical stability and high corrosion resistance. These semiconductors with relatively high activation energy and negative temperature coefficient are interesting as sensitive elements in uncooled bolometers [8]. Attractive magnetic properties (large coercivity, magneto-crystalline anisotropy and magnetostriction [9]) make cobalt–iron spinel oxides, especially in thin films form, potential candidates for magnetic devices. In addition, spinel cobaltites are

also of interest for various applications due for example to their thermoelectric [10,11], multiferroic [12,13] or catalytic [14,15] properties.

Iron cobaltites for which the composition lies between  $\text{CoFe}_2\text{O}_4$  and  $\text{Co}_3\text{O}_4$  are located in a miscibility gap of the Co–Fe–O phase diagram that leads to the precipitation of a mixture of iron-rich and cobalt-rich spinel phases at low temperature [16,17]. When its composition is in between  $\text{Co}_{1.10}\text{Fe}_{1.85}\text{O}_4$  and  $\text{Co}_{2.75}\text{Fe}_{0.25}\text{O}_4$ , a pure spinel can be easily obtained by annealing this oxide at 900 °C and quenching down to room temperature to avoid the phase separation [18,19]. It is itself a first challenge to deposit a pure and metastable spinel oxide thin film in the miscibility gap area without any thermal treatment requirement. From this pure spinel pristine phase obtained in the miscibility gap of the phase diagram, it is then possible to obtain self-organized materials by spinodal decomposition at low temperature [20]. Such a spontaneous transformation has a great interest because it can promote a regular alternation, at nanometric scale, of magnetically ordered phases made of iron-rich and cobalt-rich spinel oxides [21–24]. The study of spinodal decomposition of magnetically ordered phases could lead to original properties. For example giant magnetoresistance was thus observed in ferromagnetic alloys obtained from spinodal decomposition [25,26]. Other collective properties could be generated in these potential self-organized metamaterials to get for instance magnonic crystals [27,28].

In this study, spinel thin films were prepared by radio-frequency magnetron sputtering from a  $\text{Co}_{1.75}\text{Fe}_{1.25}\text{O}_4$  ceramic target. The composition was chosen to be close to the centerline of the miscibility gap observed in the  $\text{CoFe}_2\text{O}_4$ – $\text{Co}_3\text{O}_4$  phase diagram. We particularly studied

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the influence of deposition pressure on structure, microstructure and physical properties of films in order to get pure metastable phase at room temperature.

## 2. Experimental

### 2.1. Films preparation

Thin films were deposited by magnetron radio-frequency (RF) magnetron sputtering using a  $\text{Co}_{1.75}\text{Fe}_{1.25}\text{O}_4$  ceramic target, which has been elaborated from mechanical mixture of  $\text{Co}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4$  commercial powders. The powder mixture was pressed in a die and the green disc (20 cm in diameter and 5 mm thick) was slowly heated to eliminate the organic binder and then sintered at 900 °C for 12 h under air atmosphere. After a second heat treatment carried out at 950 °C for 4 h under air, the target density was close to 60% and the final diameter was 19 cm. The composition of the target was checked by plasma emission spectroscopy carried out in a small representative pellet prepared at the same time. The analysis of the chemical composition of the films by electron probe micro-analysis (using a Cameca SX 50 apparatus) confirmed the conservation into the film of the cationic composition of the target: all the samples showed a constant cationic ratio Co/Fe closed to 1.4 regardless of the deposition pressure.

The sputtering apparatus is an ALCATEL CIT model SCR650 equipped with a radio-frequency-generator (13.56 MHz) device as well as a pumping system (a mechanical pump coupled with a turbo molecular pump). Both target and substrate were continuously water cooled. The RF power was fixed at 1.3 W/cm<sup>2</sup> and the pressure inside the deposition chamber was lower than  $5.10^{-5}$  Pa before deposition. Pre-sputtering by argon plasma was performed during 15 min to clean the surface of the target of any impurities prior to the film deposition. Pre-cleaned 1 mm thick microscopy slides were used as substrates. In this work, P0.5D6, P1.0D6 and P2.0D6 designations refer to samples produced with an argon pressure of 0.5, 1.0 and 2.0 Pa respectively, and a target-to-substrate distance fixed at 6 cm.

For all the films, the deposition rates (Table 1) were calculated from the deposition times and thickness measurements using a DEKTAK 3030ST mechanical profilometer. Film thicknesses were set at 300 nm for all the characterizations. For magnetic measurements, the deposition was made on both faces of thinner glass substrate (0.1 mm).

### 2.2. Characterizations

Structural characterizations of films were performed at room temperature by grazing angle X-ray diffraction ( $\alpha = 1$  deg.) on a Siemens D 5000 diffractometer equipped with a Brucker Sol-X detector. The X-ray wavelength was that of the copper  $K_{\alpha}$  ray ( $K_{\alpha 1} = 0.15405$  nm and  $K_{\alpha 2} = 0.15443$  nm).

Raman spectra were collected under ambient conditions using a LabRAM HR 800 Jobin Yvon spectrometer with a laser excitation wavelength of 632.8 nm. Spectra acquisition was carried out for 400 s using  $\times 100$  objective lens and 600 g/mm grating. During the measurement, the resulting laser power at the surface of the sample was adjusted to 0.7 mW to avoid the transformation of the ferrite thin film (especially to avoid spinodal decomposition). Examination of multiple spots showed that the samples were homogeneous.

**Table 1**  
Deposition parameters.

Target diameter (cm)	19
Target-to-substrate distance (cm)	6
RF power density (W/cm <sup>2</sup> )	1.3
Sputtering gas	Ar
Background pressure (Pa)	$5.10^{-5}$
Working pressure (Pa)	0.5–1.0–2.0
Film thickness (nm)	300

To study the microstructure of the films, Atomic Force Microscopy (AFM) Veeco Dimension 3000 equipped with a super sharp TESP-SS Nanoworld©tip (nominal resonance frequency 320 kHz, nominal radius curvature 2 nm) was used. The microstructure of the samples was also investigated by scanning electron microscopy (SEM) with a JEOL JSM 6700F apparatus with a field emission gun.

Magnetic measurements were done at 300 K, 150 K and 5 K after a field cool with a superconducting quantum interference device (SQUID) magnetometer MPMS Quantum Design 5.5. The maximal applied field for the measurements was 70 kOe. The magnetizations of the samples were corrected for substrate contribution.

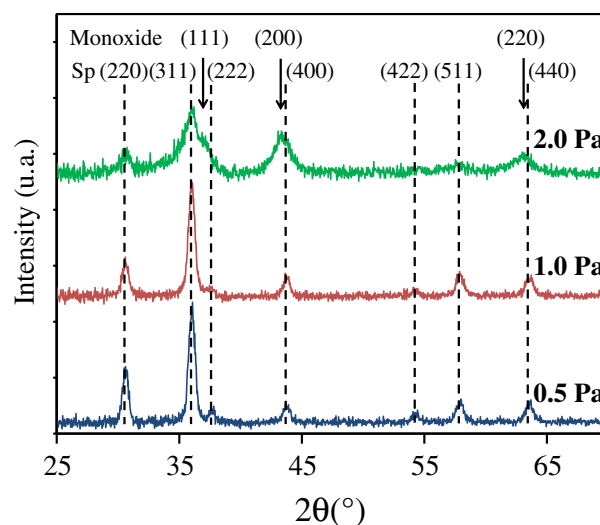
Films resistivity was determined by a four point measuring device composed of a source measure unit KEITHLEY 237, a high temperature four point probe QUAD PRO Resistivity System and a temperature controller SIGNATONE model S-1060R. This type of generator can measure a maximum resistance of  $10^{10}$   $\Omega$ .

## 3. Results and discussion

### 3.1. Structural characterizations

Fig. 1 shows X-ray diffraction patterns of iron cobaltite thin films deposited at different argon pressures. The patterns of all the films deposited at 0.5 and 1.0 Pa show the diffraction lines corresponding to cubic spinel structure without any secondary or impurity phases. However, film deposited at 2.0 Pa consists of two phases: a spinel phase and a monoxide phase with wüstite structure. Both CoO and FeO have wüstite structure with two lattice parameters very close each other:  $a = 4.2612$  Å for CoO (PDF #48-1719) and  $a = 4.3260$  Å for FeO (PDF #89-0687). Phase diagram of  $\text{Fe}_3\text{O}_4$ – $\text{Co}_3\text{O}_4$  system shows that spinel phase and monoxide phase can co-exist at thermodynamical equilibrium for temperatures higher than 950 °C [16,17]. Thus it is proposed that the monoxide phase formed in thin film deposited at 2.0 Pa is a Co–Fe mix monoxide ( $\text{Co}_y\text{Fe}_{1-y}$ )O. The formation of a composite monoxide/spinel oxide is in good agreement with the results reported by B. Mauverny et al. [29] in which the FeO/ $\text{Fe}_3\text{O}_4$  nanocomposite films were deposited from a magnetite target at high argon pressure.

Formation of a monoxide phase in thin films deposited at high argon pressure can be explained by sputtering principle [30,31]. During the sputtering at high argon pressure, target is submitted to intense bombardment by high energy  $\text{Ar}^+$ , which leads to a local overheating of target surface. Such target, in a low oxygen partial pressure, tends to exhibit a reduction on its extreme surface [32]. In addition, a high



**Fig. 1.** X-ray diffraction patterns of thin films deposited at different argon pressures (sp = spinel).

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