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ORIGINAL PAPER

Magnetic and Structural Characterization of IrO_2 and Co : IrO_2 Samples Synthesized via Pechini Method

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Abstract Diluted Magnetic Oxide Semiconductors (DMOS) are oxides that combine two important properties for applications in spintronics: the capacity to control conductivity and ferromagnetism. Obtaining new materials that exhibit simultaneously these behaviors is challenging. In this paper, we investigate whether it is possible to use IrO_2 and Co : IrO_2 as a DMOS by studying their magnetic and structural characteristics. The samples were synthesized by the Pechini method, and characterized by X-ray diffraction and magnetization measurements. These samples were doped with 0 to 10 mol% Co concentrations. The X-ray diffraction was analyzed using the Rietveld refinement procedure which showed that all cobalt (Co^{2+}) introduced into the IrO_2 lattice replace Ir^{4+} ions until the dopants concentration of about 10 mol%, and no phase segregation was observed for the highest dopant concentration investigated. Magnetization measurements as a function of temperature and applied magnetic field were performed on these samples. The results show a paramagnetic behavior, despite of the high Co concentration.

Keywords Iridium dioxide · Cobalt doped iridium oxide · Pechini method

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1 Introduction

Nowadays, the production of materials that can be used simultaneously for magnetic recording and information processing has become an important challenge. Many efforts have been made to obtain novel ferromagnetic materials with high Curie temperatures for multifunctional spintronic applications. Despite these efforts, room temperature ferromagnetism in DMOS doped with 3d cations are still not fully understood. These materials possess a special feature, the possibility of obtaining other materials with ferromagnetic phase at room temperature and with semiconducting properties. Recently, many papers have been published which point out the usage of ZnO [1, 2], TiO_2 [3], CeO_2 [4, 5], and other oxides doped with magnetic impurities [6], to achieve such properties. Fernandes et al. [7], using magnetization measurements and band-structure calculations studying CeO_2 observed magnetic moments associated with the point defects in the oxide structure. On the other hand, few of the authors in the literature mention magnetic properties of IrO_2 doped with cobalt, and furthermore, papers authors were interested in other properties of those materials [8]. Otherwise, from a fundamental point of view, the Co : IrO_2 system could be a candidate to a DMOS. Considering the importance of DMOS, in this work, we present a preliminary investigation about samples of IrO_2 doped with Co obtained by Pechini method [9, 10] which was chosen to maximize doping homogeneity distribution and stoichiometry control.

2 Experimental

2.1 Sample Synthesis

The precursor solution of IrO_2 was prepared using the Pechini method [9, 10]. Anhydrous citric acid (P.A. Synth) was

added to ethylene glycol (P.A. Mallinckrodt) and kept under stirring at 70 °C for 10 min. This period was enough to completely dissolve the citric acid. Afterward, the Ir salt ($IrCl_3 \cdot 3H_2O$—99.9%—Alfa Aesar) was slowly added to the acid, while maintaining both temperature and stirring, until the compound was completely diluted. In order to prepare the doped samples, $CoSO_4 \cdot 7H_2O$ (P.A. Synth) was added to the solution described above, also under stirring at 70 °C for 15 min. The materials were prepared with 0, 2.5, 5, and 10 mol% of cobalt ions. The solutions were then polymerized at 110 °C for 60 min and calcined for 120 min each in three sequential stages: at 300 °C, at 500 °C and finally at 700 °C. After calcination, powdered samples were obtained without aggregate formation.

2.2 Sample Characterization

The samples were characterized by XRD (X-ray diffraction) using an (Rigaku 12500PC) equipment with Cu K_α (1.54 Å) radiation. A step scan was used with 0.02 ° resolution at a range of 5–120 ° and the Rietveld refinement [11], using GSAS-EXPGUI [12, 13] software, was carried out for a detailed analysis. Magnetic characterization was performed using a SQUID magnetometer (Quantum Design MPMS-5S). Magnetization measurements as a function of applied magnetic field were performed at up to 50 kOe at a temperature of 5 K. Magnetization measurements as a function of the temperature were done using the Field Cooling (FC) protocol with the temperature ranging from 2 to 300 K.

3 Results and Discussion

Figure 1 shows X-ray diffraction patterns of samples with 0, 2.5, 5, and 10 mol% of Co. Pure IrO_2 shows a intense

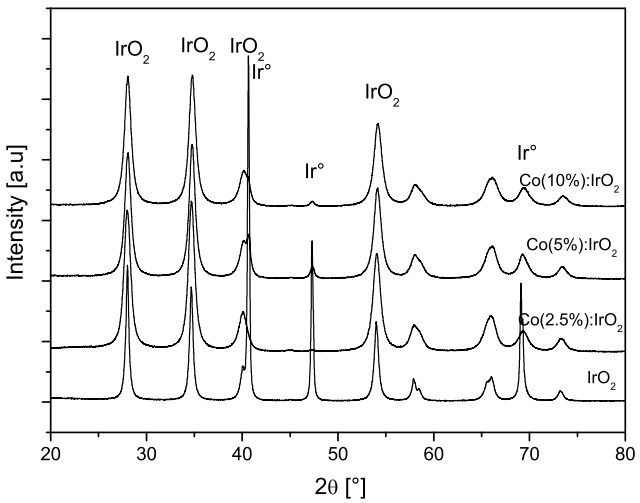

Fig. 1 X-ray diffraction pattern of Co : IrO_2 samples with 0, 2.5, 5, and 10 mol% of cobalt

Table 1 Values of metallic Ir percentage, IrO_2 lattice parameter and crystallite size obtained from Rietveld refinement for Co : IrO_2 samples

mol% Co	mol% Ir	IrO_2 a = b = [Å]	IrO_2 c [Å]	D [nm]
0	42	4.509	3.161	28.08
2.5	0.68	4.504	3.155	14.61
5	6.80	4.502	3.153	14.95
10	3.10	4.498	3.146	13.69

diffraction peak for Ir in the metallic phase in which the Rietveld refinement was calculated at 42%. For the doped samples, the metallic portion of iridium decreases in an important amount. It is relevant to emphasize that even with 10 mol% of Co none of the following phases, CoO, Co_2O_3, or Co_3O_4, were detected. These information are summarized in Table 1, where the first column shows the Co percentage in each sample, the second column shows the percentage of metallic iridium; the third and fourth columns presents lattice parameters obtained from IrO_2 in synthesized samples; and the last column presents de crystallite size. However, as Co doping level increases, an inhibition of metallic iridium formation is noticed. Besides, for the doped samples, there is a decrease in the crystallite size (D).

This result indicates that Co^{2+} ions could replace ions Ir^{4+} in the IrO_2 lattice. Comparing the theoretical values of the IrO_2 lattice structure and the samples described in Table 1, a small distortion in the lattice is observed. This is an indication that the doping with Co is homogeneous, with Co^{2+} ions substituting ions Ir^{4+} in up to 10 mol% of cobalt. These results are very important, since in general, there is a segregation phase for dopant concentrations above 5 mol% [14] due to the differences in ion size, crystalline structure, and ion charge. In our case, the segregation phase was indeed observed when Co doping level was higher than 15 mol% (data not shown). It is also evident that the doping with Co inhibits the crystallite growth.

Magnetization measurements as a function of applied magnetic field were performed at 5 K, as shown in Fig. 2. All samples present a paramagnetic behavior. However, a small remanent magnetization was observed for the Co (10 mol%) : IrO_2 sample. Besides, this last sample had a detectable coercive field of about 40 Oe, as shown in the inset of Fig. 2. As the Co concentration increases, the magnetization also increases. Finally, it is important to stress that sample Co (10 mol%) : IrO_2, presents 10 times more magnetic moments compared to the pure IrO_2 sample.

Figure 3 shows magnetization curves as function of temperature at 100 Oe. Although it is expected that the introduc-

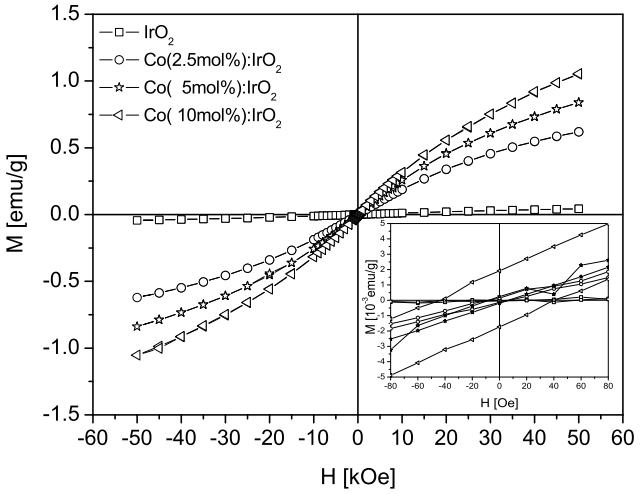

Fig. 2 Magnetization measurement in function of applied magnetic field in Co : IrO_2 samples with 0, 2.5, 5, and 10 mol% of cobalt, at 5 K. The *inset* shows the region of low fields

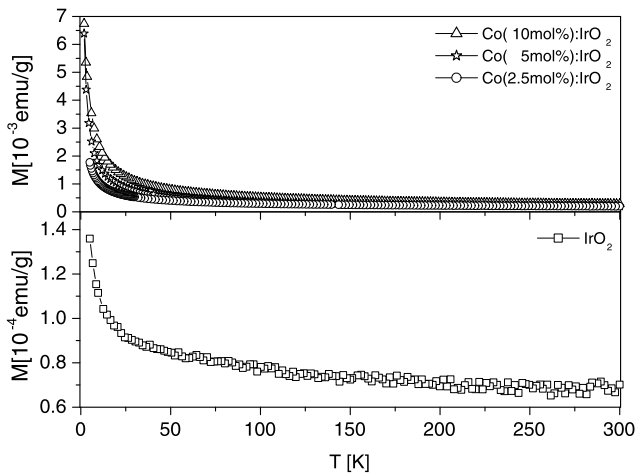

Fig. 3 Magnetization measurement in function of temperature for Co : IrO_2 samples with 10, 5, and 2.5 mol% of cobalt and IrO_2, at 100 Oe

tion of Co dopant in IrO_2 material leads to an appearance of a ferromagnetic phase, in our samples this phase was not detected. As observed in the CeO_2 system case, the most important contribution for the establishment of ferromagnetic phase is the presence of Ce and O vacancies [7]. In the present case, one possible explanation for the absence of a ferromagnetic phase is that the Co ions are introduced in the IrO_2 lattice as substitutional ions, not allowing the onset of ferromagnetism.

4 Conclusions

In this paper, we studied the structural and magnetic properties of IrO_2 and Co : IrO_2 samples synthesized via Pechini method. Regarding structural features, it is evident that up to 10 mol% of dopant ions were accommodated in the crystal structure of IrO_2 replacing Ir^{+4} in the lattice. The magnetic characterization revealed that all samples exhibited a predominant paramagnetic behavior.

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