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MAGNETIC, STRUCTURAL AND MORPHOLOGICAL STUDY OF $LaCoO_3$ THIN FILMS

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Abstract

The $LaCoO_3$ belongs to the class of compounds called Mott insulators. These oxide perovskite-type cobaltites with p-type are considered alternative materials to improve the efficiency of the process of conversion of energy in thermoelectric devices. The interest in $LaCoO_3$ is mostly related to its non-magnetic ground at low temperature. We have fabricated $LaCoO_3$ thin films via an RF magnetron sputtering technique using high-oxygen pressure at 600°C on (100)-Si substrates. The target for the growth of the films was prepared by a solid state reaction method. The crystalline structure of the films was determined by X-ray diffractometry showing that the $LaCoO_3$ main peaks correspond to the (001) preferential orientation. X-ray measurements also indicated that the formation of $LaCoO_3$ was complete, and it was verified that a pure phase with rhombohedral crystalline structure was obtained. The film surfaces were characterized by atomic force microscopy (AFM) in the non-contact mode. AFM micrographs showed homogeneous surfaces in the films with average roughness values of 1.06 nm, and 3.49 nm for samples with 40 nm and 120 nm of thickness respectively. The magnetic properties of the samples were characterized via isothermal hysteresis curves, between 100 and 300K, using a vibrating sample magnetometry (VSM) technique. The curves showed a hysteretic behavior with a saturation field that decreases with the increasing of temperature.

***Keywords**: Cobaltites, magnetic properties, structural properties, Perovskites, Thermoelectrics,*

1. INTRODUCTION

The $LaCoO_3$ is a compound classified as Mott insulating, and the study of this material has attracted much attention from the aspect of the anomalous spin-state transition. The interest in studying the $LaCoO_3$ is the behavior of its non-magnetic ground state at low temperatures [1-6].that transforms with temperature showing a standard Curie-Weiss behavior. This phenomenon is attributed to the temperature induced transformation [6-9]. from the low-spin (LS) (S=0) to the intermediate (IS) (S=1) or/and high-spin (HS) (S=2) state of the trivalent cobalt ion. In current approaches the orbital moment is neglected [8-10]. . The magnetic and transport properties of $LaCoO_3$ have temperature dependencies due to thermally induced behavior in the electronic arrangement of Co^3 ions [11]. The state ground is the low spin (LS), t^6_{2g}, S=0, and with increasing of the temperature, a crossover into a magnetic, but still insulating state, appears at about 80-120 K. The HS state is reported to be located at approximately 0.01-0.08 eV above the LS state.

Perovskites-type phases show a variety of useful properties, an enormous variability, and high potential for energy conversion process [12].

Depending on their composition, they reveal insulating, p or n-type semiconducting, metallic or even superconducting transport properties. Regarding the lanthanum cobalt oxide phases, A-site and B-site substitution can improve their thermoelectric properties by changing the oxidation state of Co.

In perovskite material were the B (ABO_3-general formula of perovskite structure) site is occupied by an ion with unpaired *d* electrons, such as Fe^3, Mn^3, Cr^3, Co^3 or Co^2, magnetic ordering can occur [13].. The $LaCoO_3$ perovskite also receive attention as potential candidate for thermoelectric (TE) applications.

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The high temperature stability and isotropic crystal structure of $LaCoO_3$ also offer an advantage in designing high temperature TE devices and eliminates the need of epitaxial growth in preparing thermoelectric elements [15].
In this work, we report a study of magnetic properties, structural and morphological characteristics of $LaCoO_3$ thin films grown onto Si substrates with (100) orientation.

1. EXPERIMENTAL DETAILS

The $LaCoO_3$ target was prepared by a solid state reaction method [14].. The target was synthesized by the following procedure. Starting materials of La_2O_3 and Co_3O_4, were mixed homogeneously in stoichiometric ratio. The mixed powders of starting materials were calcined about 1000°C for 24 hours in air, furnace cooled to room temperature. The reacted powders were then reground and pressed in disk form. The disks were sintered at 1100°C for 96 hours in air and then cooled to room temperature

Thin films of $LaCoO_3$ were deposited onto Si (100) substrates by an rf magnetron sputtering technique at high oxygen pressure. Thicknesses of $LaCoO_3$ films were determined by the determination of the deposition rate, and controlling deposition time. A deposition rate of 1.3 nm/min was achieved for $LaCoO_3$ films.

Phase purity of the $LaCoO_3$ in bulk form (powder samples) and structural characterization of $LaCoO_3$ films grown on Si (100) substrates was confirmed by X-Ray diffraction (XRD) measurements.

$LaCoO_3$ thin films surfaces were characterized by atomic force microscopy-AFM (We used an Asylum Research MFP-3D^{TM} Standard Alone Atomic Force Microscope /Cantilever Olympus AC240TS) in the non-contact mode.The magnetic properties of the samples were characterized via isothermal hysteresis curves, between 100 and 300 K, using a vibrating sample magnetometry (VSM) technique of Physical Property Measurement System-*PPMS* of Quantum Design. The basic measurement is accomplished by oscillating the sample near a detection (pickup) coil and synchronously detecting the voltage induced. By using a compact gradiometer pickup coil configuration, a relatively large oscillation amplitude (1.3 mm peak) and a frequency of 40 Hz, the system is able to resolve magnetization changes of less than 10^{-6} emu at a data rate of 1 Hz.

3. RESULTS AND DISCUSSION

The powder X-ray diffraction experiment at room temperature (figure 1) show then the $LaCoO_3$ bulk sample crystallize in the rhombohedral structure, moreover the characteristic peaks of $LaCoO_3$ are distinguished.

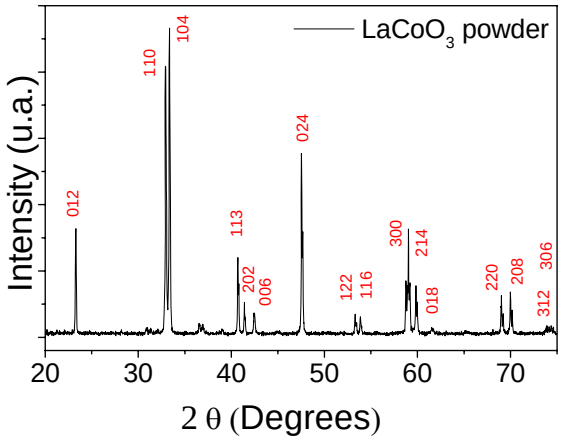


Figure1. X-ray diffraction spectrum of a $LaCoO_3$ powder sample

The measurements of X-Ray were performed in the range of 2θ: 20-75 degrees. At high temperature (>1700K), the structure of $LaCoO_3$ is cubic [17]. . By lowering the temperature and the structure becomes rhombohedral .
The structural characterization of a $LaCoO_3$ thin film grown on Si substrate and with thickness of 53 nm is shown in figure 2. In this figure is contrasted the spectrum of $LaCoO_3$ bulk and $LaCoO_3$ thin film.

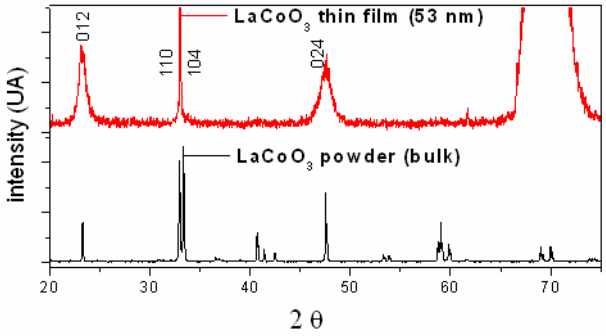


Figure 2. X-ray diffraction spectrum of $LaCoO_3$ powder and $LaCoO_3$ thin films of 53 nm of thickness.

The peaks corresponding to the orientations: (012), (110), (104), and (024) which are present in spectrum of the bulk material are also presenting in the X-ray diffraction spectrum of $LaCoO_3$ thin film of 53 nm of thickness.

$LaCoO_3$ AFM micrograph (figure 3a) show

homogeneous surface in the films with average roughness values of 1.06 nm, for the sample with 53 nm of thickness. We can observe a comparison of this surface type with other surface of the same material (figure 3b) but with 120 nm thickness, in this case we see an homogeneous surface with an average roughness value of 3.49 nm .

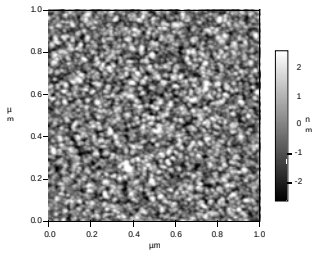


Figure 3a. AFM image of a $LaCoO_3$ thin film with 53 nm of thickness

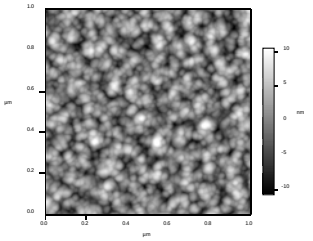


Figure 3b. AFM image of a of $LaCoO_3$ thin film with a 120 nm of thickness

These samples show different grain height: 1.5 nm and 9 nm for the surfaces of 53 and 120 nm of thickness respectively. In figure 4 we can observe the magnetization curve as function of temperature. The curve shows a typical Curie-Weiss behavior indicating a non-magnetic order at low temperatures. This behavior is confirmed by the magnetization as function of magnetic field curves at different temperatures (Figure 5). In this figure we observe practically a non-hysteretic behavior, with a dependence of the saturation magnetization with the temperature. The saturation decreases with the temperature increasing. The magnetic behavior is show in the typical plot of magnetization as a function of magnetic field (M-H loop) measured to different temperatures: 100, 150, 200 and 300K (figure 5). for $LaCoO_3$ samples in thin film form. It exhibits hysteresis behavior . its behavior is related with the ferromagnetic type. The magnetization loops show saturation for momentum magnetic values of 144, 123 and 103 emu/cm^3 for 150, 200 and 300 K respectively, and for H=0 the magnetic moment is 12, 11 and 8 emu/cm^3 for 150, 200 and 300 Oe of magnetic field

The magnetization loop for 100 K could not be satured to a field of 5000 Oe and indicates the presence of competing magnetic interaction. The magnetic hysteresis of the $LaCoO_3$ thin films reflects the order and motion of the magnetic domains of the deposited layer.

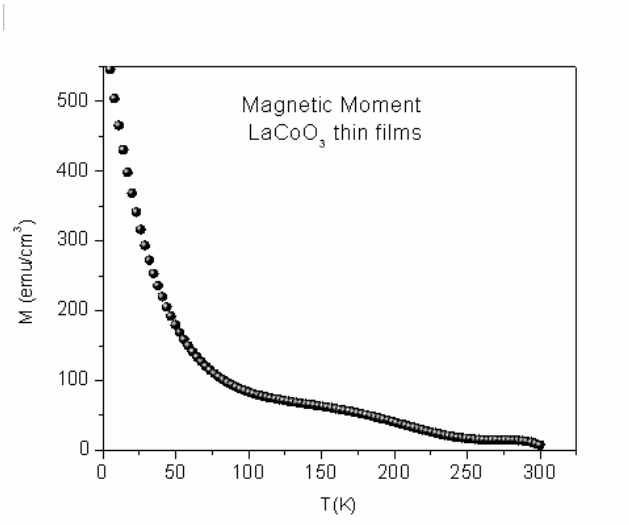


Figure 4. Magnetic moment in function of temperature for $LaCoO_3$ in thin films form

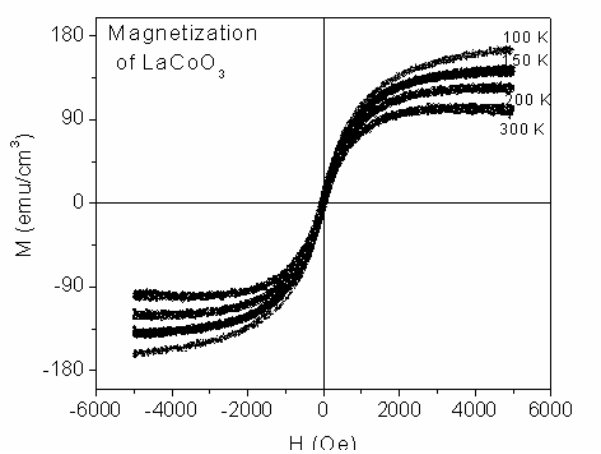


Figure 5: Magnetization curves of $LaCoO_3$ thin films for different temperatures (100, 150, 200 and 300K)

4. CONCLUSIONS

We have grown $LaCoO_3$ thin films on single crystal substrates of Si with (100) orientation. The x-ray measurements show that the films were polycrystalline with preferential orientations of (012), (110), (104), and (024) of the rhombhoedral phase. The deposited thin films show good uniformity in the surfaces with average roughness value of 1.06 nm and a grain height of 1.5 nm.

Magnetically the $LaCoO_3$ films showed a paramagnetic behavior as observed by magnetization measurements as function of temperature and magnetic field.

5. ACKNOWLEDGEMENTS:
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