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Preparation and electron correlation effects of the perovskite $La_{0.8}Ca_{0.1}Pb_{0.1}Fe_{1-x}Co_xO_3$ ($0 \leq x \leq 0.20$)

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ABSTRACT

The nano-materials$La_{0.8}Ca_{0.1}Pb_{0.1}Fe_{1-x}Co_xO_3$ (x = 0.00 to 0.20) were prepared by the sol-gel method and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray dispersion (EDS). The structure refinement of the XRD data was performed using the Rietveld method. These compounds were found to exhibit a single phase and crystallize in the orthorhombic structure with *Pnma* space group. The chemical analysis by EDS shows the successful incorporation of Co (Cobalt) in the parent sample. The volume was found to decrease with the increase of the cobalt-content. The volume decrease was also investigated theoretically by comparing the total energies of $LaFeO_3$ and $LaCoO_3$ compounds which were calculated within density functional theory (DFT). We find an almost agreement between experimental and theoretical results, provided we use the correct SGGA + U functional (in contrast to the SGGA–Spin polarized Generalized Gradient Approximation), which takes properly into account the strong electron correlation in the open *d*-shell by a Hubbard-like U term. Our analysis of the corresponding densities of states indicates a qualitatively different ground state behavior of the Fe- or Co-ion.

1. Introduction

Materials with the perovskite structure present a chemical formula ABO_3 and are composed of a rare-earth cation in the A-site and a transition metal cation in the B-site. They are the subject of intense research, both of fundamental and of applied character. Particularly, $LaFeO_3$-based oxides have been widely studied because they are potential candidate materials for various applications, such as chemical sensors [1–3], catalysis [4], solid oxide fuel cells [5] and magnetic materials [6]. For instance, several studies were carried out in order to understand the correlation between the structural, electrical and catalytic properties of $La_{1-x}M_xFeO_3$ and $LaFe_{1-x}M_xO_3$ (M = Pb, Mg, Ba, Co…), i.e. of A and B-sites doped $LaFeO_3$ [7–9]. Of special interest are the gases sensing properties of these compounds, for ethanol and other gases.

However, the insertion of cobalt in the B-site of $La_{0.8}Ca_{0.1}Pb_{0.1}Fe_{1-x}Co_xO_3$ compounds was not investigated up to now in sufficient detail. At first sight, the cobalt is just supposed to improve the gas sensitivity of the material. That was indeed experimentally shown in [10] for the case of NH_3 sensing by detailed measurements of the electrical conductivity of that material under exposure to several gases. The utility of Co-doping on the B-site of the perovskite is based on the valence fluctuations of Co in contrast to the stable valence of Fe. However, a profound analysis of Co-doping in that compound is missing up to now. Also, as we will show below, the clarification of the structural properties of these mixed crystals contributes to the fundamental understanding of these materials, since there are important differences between $LaFeO_3$ and $LaCoO_3$. $LaFeO_3$ is known to be a magnetic insulator whose magnetic structure is dominated by nearly antiparallel magnetic moments on neighboring Fe sites with a small canting angle leading to weak ferromagnetism and a Curie temperature of 670 K. The situation in $LaCoO_3$ is not as simple. It is known to be a diamagnetic insulator below 80 K and a paramagnetic metal above 600 K with a paramagnetic insulator phase in between. The theoretical description of its electronic and magnetic properties is highly disputed with approaches based on the single-ion picture including spin-exchange [11, 12], band structure calculations with electrons interacting via static mean field [13, 14] or by dynamical mean-field theory [15, 16], or even on the concept of exciton condensation [17]. By comparing structural analysis with ab-initio calculations, we show below a fundamental difference between the Fe and the Co ions in the given perovskite, which can only be described by a proper treatment of the strong electron correlation in the incompletely *d*-shell of the transition metal ion.

In many literature reports, the $LaFeO_3$ compound and its derivatives

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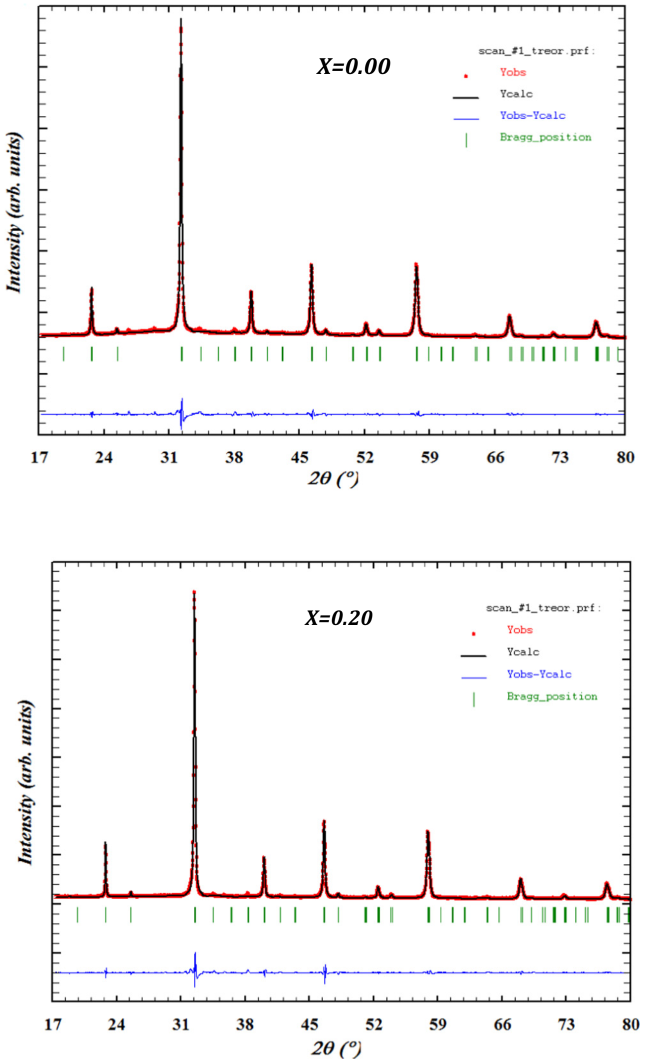

Fig. 1. XRD patterns of $La_{0.8}Ca_{0.1}Pb_{0.1}Fe_{1-x}Co_xO_3$ (x = 0.00 and 0.20) compounds.

Table 1
Structural parameters of $La_{0.8}Ca_{0.1}Pb_{0.1}Fe_{1-x}Co_xO_3$ doped with different concentrations of cobalt (x = 0.00 to x = 0.20).

Sample	Unit cell parameters			Volume (Å^3)
	a (Å)	b (Å)	c (Å)	
x = 0.00	5.526	7.840	5.543	60.052
x = 0.05	5.533	7.830	5.517	59.768
x = 0.10	5.537	7.802	5.525	59.681
x = 0.15	5.517	7.804	5.500	59.215
x = 0.20	5.510	7.792	5.493	58.965

are prepared by different processes including sol-gel [18], citric acid [19], co-precipitation [20] and thin films [21]. In the present work, $La_{0.8}Ca_{0.1}Pb_{0.1}Fe_{1-x}Co_xO_3$ (x = 0.00, 0.05, 0.10, 0.15 and 0.20) nanocrystalline powder has been prepared by the sol-gel method [22]. Thus, it is important to understand the effects of replacing some of the Fe ions by Co ones on the structural properties of $La_{0.8}Ca_{0.1}Pb_{0.1}Fe_{1-x}Co_xO_3$ (x = 0.00, 0.05, 0.10, 0.15 and 0.20). The structural properties are investigated here by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). For a deeper understanding, we investigate the effect of Co-doping on the structural properties of $LaFe_{1-x}Co_xO_3$ compounds using a density functional theory (DFT) study. Neglecting the small concentrations of Ca and Pb and comparing $LaFeO_3$ with $LaCoO_3$, we are able to show that the influence of the strong electron correlation in the incompletely filled d-shell is already visible on the level of the lattice contraction by Co-doping. In detail, we compare the local spin-density approximation (LSDA), with the spin resolved version of the generalized gradient approximation (SGGA), and with the SGGA + U method, which treats explicitly the Hubbard U term. By comparing with our experimental data, we are able to show that only the SGGA + U method can properly describe the volume decrease by Co-doping. We also analyze the densities of states, which indicate a stable valence of +3 for the Fe ion but valence fluctuations for the Co one. We show that just this different behavior of the Fe- and Co-ion is responsible for the considerable volume decrease by Co-doping.

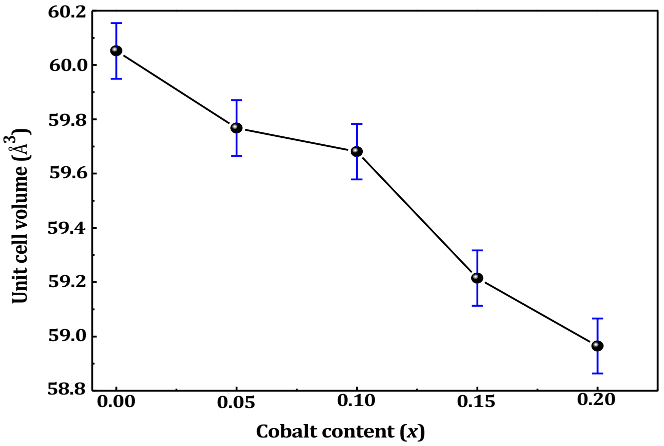

Fig. 2. Variation of the unit cell volume as a function of the cobalt content (x) of $La_{0.8}Ca_{0.1}Pb_{0.1}Fe_{1-x}Co_xO_3$ (x = 0.0, 0.05, 0.10, 0.15 and 0.20) compounds.

2. Experimental method

Powders of the perovskite $La_{0.8}Ca_{0.1}Pb_{0.1}Fe_{1-x}Co_xO_3$ (x = 0.00, 0.05, 0.10, 0.15 and 0.20) were prepared by the sol-gel method. This technique is recognized to achieve fine particle and nano-structured materials. Stoïchiometric amounts of lanthanum nitrate, lead nitrate, calcium nitrate, ferric nitrate and cobalt nitrate were used as precursor starting materials. The experimental method was described in our previous work [10]. The phase analysis of the samples was performed by X-Ray Diffraction at room temperature. Cell parameters and volume were obtained by the Rietveld structural refinement of the experimental data of XRD using the Rietveld structural refinement FULLPROF software [23]. The microstructure and chemical composition of the nanoparticles samples was examined by scanning electron microscopy (SEM) and by energy dispersive X-ray spectroscopy (EDS).

3. Theoretical method

The total energy and the densities of states of the $LaFeO_3$ and the $LaCoO_3$ compounds were determined by the Vienna ab-initio simulation package (VASP) [24], which is based on density functional theory (DFT). The calculations had been performed by the local spin density approximation (LSDA), the spin generalized gradient approximation (SGGA) of Perdew and Wang (PW91) [25] and by taking into account the strong electron correlation in the incompletely filled 3d shell of Fe