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Synthesis and characterization of calcium-doped lanthanium nickelates $La_{2-x}Ca_xNiO_{4+\delta}$ ($x = 0, 0.02, 0.1, 0.275, 0.333, 0.5$)

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Abstract

We have investigated the influence of Ca doping on chemical and physical properties of the $La_2NiO_{4+\delta}$ compounds. Several Ca-doped compounds were then prepared by the citrate method. The X-ray diffraction analysis indicates that all the obtained compounds are pure with no presence of secondary phases. All compounds adopt a tetragonal structure with I4/mmm space group. As x increases, the excess oxygen δ decreases. Magnetic susceptibility shows anomaly below 200 K, which was attributed to charge ordering. Magnetization measurements displayed prominently the presence of weak ferromagnetism below 200 K. Most probably, the ferromagnetic component modifies the antiferromagnetic fluctuations in the NiO_2 planes. The origin of the ferromagnetic component must be related to a presence of kind of bond-centered stripes.

Keywords: Charge and spin ordering; Stripes; $La_2NiO_{4+\delta}$; Oxygen non-stoichiometry; Ca-doping; Magnetic susceptibility

1. Introduction

The nickelates $R_{2-x}A_xNiO_{4+\delta}$ are iso-structural with superconductors cuprates $La_{2-x}A_xCuO_4$ ($A =$ Ca, Sr, or Ba) [1,2] but no superconductivity was found in the materials which remain insulating up to $x = 1.0$. The magnetic, electronic and the structural properties depend strongly on the concentration and the nature of doping (holes or electrons), which have not been explored systematically. The aim of this work is to deal with some of them, especially concerning the La-based compounds.

Their structures belong to the K_2NiF_4 group, which can be described as a successive stacking of NiO_2 layers and R_2O_2 layers of NaCl type. However, due to the small size of the R ion, the R–O bonds are expanded while the Ni–O bonds are compressed. An alternated rotation of NiO_6 octahedron along the [110] direction of the ideal quadratic structure *I4/mmm* allows minimizing these structural strains by decreasing the R–O distance. The structure also relaxes due to the inserting of oxygen in the R–O layer (note that its quantity depends on the size of earth elements) [3]. As the consequences, a partial oxidation of Ni^{2+} in Ni^{3+} occurs in NiO_2 layers to satisfy the electroneutrality conservation. Thus, the phase diagram T–δ is very complex in the case of $La_2NiO_{4+\delta}$. It presents a succession of ordered domains and phase separations of the electronic origin [4]. In fact, the interstitial oxygen influences all the properties of these phases. Magnetic and electronic properties change drastically with the value of excess oxygen δ. Tranquada et al. had shown by neutron diffraction data of $La_2NiO_{4+\delta}$ single crystals, for $\delta > 0.105$, a 3D order of interstitial oxygen takes place and it is related to a particular distribution of charges and spins [5]. For $La_{2-x}Sr_xNiO_4$ compound, as $x = 1/3$ and $1/2$, magnetic and resistivity anomalies, which have been already observed by S.W. Cheong et al. [6], have been attributed to the charge order. This phenomenon have been also confirmed by resistivity measurements and optic spectroscopy by Katsufuji et al., for $x = 1/3, 1/2$ [7].

The combined order of holes and spins is proved to be a common phenomenon in the cuprates and nickelates. The order can be described as a stripes phase, where the holes are segregated in domains walls separating the non-doped antiferromagnetic domains periodically. Stripe phases have been observed in Sr [8], Zn [9] and oxygen-doped La_2NiO_4 [10]. The

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first observation of the unusual magnetic correlation in the nickelates was done by Hayden et al. [11] by neutron diffraction on $La_{1.8}Sr_{0.2}NiO_{3.96}$ crystals. On the other hands, the existence of a hole order in $La_{2-x}Sr_xNiO_4$ has been confirmed by electron diffraction [11] and transport measurements on ceramics [6]. A combined order of Ni spins and holes generated by doping in $La_2NiO_{4+\delta}$ also exists for $\delta = 0.133$ [12]. In this work, we were interested in $La_2NiO_{4+\delta}$, in order to investigate the influence of Ca-doping on the rare earth site and the excess oxygen on structure and magnetic properties. In this article, we present the methodological synthesis of various $(La,Ca)_2NiO_{4+\delta}$ compounds as well as structural, chemical and magnetic characterizations.

2. Experiment

Poly-crystals of $La_{2-x}Ca_xNiO_{4+\delta}$ ($x = 0, 0.02, 0.1, 0.275, 0.333, 0.5$) were prepared by the modified citrate method [13]. This method consists of a heat treatment of a precursor formed by an organic polymerization of a citrate. The gel was then fired in a ventilated furnace for 5 h at 650 °C.

The obtained powder was vigorously ground and annealed in air at 1100 °C for 12 h. The excess oxygen δ was deduced from a thermogravimetric analysis with a heating rate of 2 °C/min in a flowing mixture of approximately 20% H_2 and 80% Ar. The cation distribution is observed by a scanning electron microscopy (SEM) combined with the energy dispersive spectroscopy (EDS).

The powder X-ray diffraction (XRD) patterns of all samples were collected at room temperature (RT) using a Rikagu diffractometer in a θ–2θ geometry. The structural Rietveld refinement was also done on these data by using to FULLPROF 2000 program [14]. DC magnetic susceptibility was carried out by a Manics Faraday-based magneto-susceptometer in the range of 70–300 K.

3. Results and discussions

3.1. X-ray diffraction

All compositions are single phase and have a tetragonal structure. The space group for $x \leqslant 0.5$ is I4/mmm. From XRD, no significant impurities have been detected. The refinement results are summarized in Table 1. The evolution of lattice parameters of $La_{2-x}Ca_xNiO_{4+\delta}$ ($0 \leqslant x \leqslant 0.5$) samples obtained at room temperature shows that the a and c parameters decrease when x increases. The removal of electron from the $d_{x^2-y^2}$ band of Ni atom in order to relieve the initial compressive stress in the Ni–O bonds causes a decrease of the a parameter. The decrease of the c parameter is due to the substitution of La^{3+} ($r_{La^{3+}} = 1.216$) by a smaller cation Ca^{2+} ($r_{Ca^{2+}} = 1.18$); then the charge compensation which allows an oxidation of Ni^{2+} ($r_{Ni^{2+}} = 0.69$) in Ni^{3+} ($r_{Ni^{3+}}$(high spin) = 0.60), $r_{Ni^{3+}}$(low spin) = 0.56) decreases the length of LaO and NiO bending. On the other hand, the structural strain correlated with the tilting angle of the NiO_6 octahedron is lowered by an introduction of extra oxygen in the rock salt layer that fills the space. The increase of the La–O bending tensile is compensated by diminishing the length of the Ni–O bending and by an introduction of extra oxygen that make the Goldsmith t factor (defined by $t = d_{R\text{–}O}/\sqrt{2}d_{Ni\text{–}O}$) increases. The data showed a decrease of the cell volume: this comportment is due to both of the substitution of a smaller Ca^{2+} for La^{3+} and an oxidation of larger Ni^{2+} to smaller Ni^{3+}. Theses results were consistent with the result reported by Tang et al. [15].

3.2. TGA–EDS

The TGA weight loss curves and the residual concentration of Ca analyzed by EDS are shown in Fig. 1. Based on those, we can determine the hole concentration (n_H) in the samples. One can note that the hole concentration is defined by $n_H = x + 2\delta$, where x is the Ca concentration and δ is the amount of the excess oxygen.

TGA curves (Fig. 1) show that there is a certain difference between doped and non-doped compounds. For $x = 0$, one observes a plateau (noted A) which corresponds to a reduction of $La_2NiO_{4+\delta}$ to La_2NiO_4. This plateau is related to the Ni^{2+}

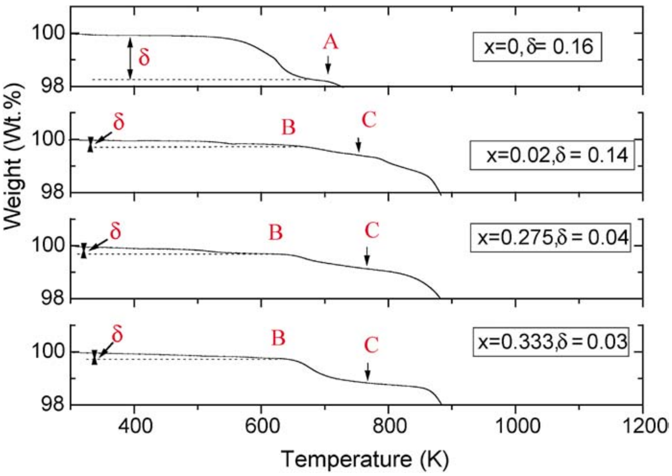

Fig. 1. TGA plots of $La_{2-x}Ca_xNiO_{4+\delta}$.

Table 1
Refined structural parameters for powders samples of $La_{2-x}Ca_xNiO_{4+\delta}$

x	a (Å)	c (Å)	V (Å^3)	R_{exp} (%)	R_{Bragg} (%)	Rwp (%)
0.02	3.8606(9)	12.6766(1)	188.935	2.91	3.02	6.10
0.1	3.8551(7)	12.6715(7)	188.321	3.52	2.95	7.8
0.275	3.8283(8)	12.6082(5)	184.784	2.84	2.72	5.14
0.333	3.8263(7)	12.6103(9)	184.622	2.86	2.02	4.56
0.5	3.8262(0)	12.6112(7)	184.626	2.87	3.05	5.5